## Contents

**Volume 65, Issue 4, October 2021**

<table>
<thead>
<tr>
<th>Page</th>
<th>Title</th>
<th>Authors</th>
</tr>
</thead>
<tbody>
<tr>
<td>504</td>
<td>Guest Editorial: Platinum Group Metals: Widespread Use As Functional Material</td>
<td>By Ulrich E. Klotz</td>
</tr>
<tr>
<td>506</td>
<td>A Conflict of Fineness and Stability: Platinum- and Palladium-Based Bulk Metallic Glasses for Jewellery: Part I</td>
<td>By O. S. Houghton and A. L. Greer</td>
</tr>
<tr>
<td>519</td>
<td>A Conflict of Fineness and Stability: Platinum- and Palladium-Based Bulk Metallic Glasses for Jewellery: Part II</td>
<td>By O. S. Houghton and A. L. Greer</td>
</tr>
<tr>
<td>535</td>
<td>Research Progress of Platinum-Based Superalloys for High Temperature Applications</td>
<td>By Changyi Hu, Yan Wei, Hongzhong Cai, Li Chen, Xian Wang, Xuxiang Zhang, Guixue Zhang and Xingqiang Wang</td>
</tr>
<tr>
<td>556</td>
<td>Study of Ultrasonic Attenuation and Thermal Conduction in Bimetallic Gold/Platinum Nanofluids</td>
<td>By Alok Kumar Verma, Navneet Yadav, Shakti Pratap Singh, Kajal Kumar Dey, Devraj Singh and Raja Ram Yadav</td>
</tr>
<tr>
<td>568</td>
<td>Mass Loss of Platinum-Rhodium Thermocouple Wires at 1324°C</td>
<td>By Sivahami Uthayakumaar, Stuart Davidson and Jonathan Pearce</td>
</tr>
<tr>
<td>574</td>
<td>Technological Capabilities of Hydrocarbonyl Processes in the Concentration and Separation of Platinum Group Metals</td>
<td>By I. V. Fedoseev, Yu. A. Kotlyar, V. V. Vasekin and N. V. Rovinskaya</td>
</tr>
<tr>
<td>584</td>
<td>Microstructure Evolution of Ruthenium During Vacuum Hot Pressing</td>
<td>By Renyao Zhang, Junmei Guo, Chuanjun Wang, Limin Zhou and Ming Wen</td>
</tr>
<tr>
<td>593</td>
<td>“Spacecraft Thermal Control Technologies”</td>
<td>A book review by Sara Gligoroska</td>
</tr>
<tr>
<td>595</td>
<td>Johnson Matthey Launches New Platinum Group Metal Award Scheme</td>
<td>By Emma Schofield</td>
</tr>
<tr>
<td>597</td>
<td>&quot;Space Robotics&quot;</td>
<td>A book review by Wolfgang Kaltner</td>
</tr>
<tr>
<td>600</td>
<td>Using Surface Science Techniques to Investigate the Interaction of Acetonitrile with Dust Grain Analogue Surfaces</td>
<td>By Emily R. Ingman, Amber Shepherd and Wendy A. Brown</td>
</tr>
<tr>
<td>615</td>
<td>Johnson Matthey Highlights</td>
<td></td>
</tr>
</tbody>
</table>
Introduction

Platinum group metals (pgms) have widespread applications as functional materials in many different industries. The applications range from catalytic surfaces or particles, sensors, biomedical imaging or drug delivery systems and thermocouples up to jewellery items that we use for special moments of our life. The pgms are used as solid bulk materials, powders, thin films, organic compounds or liquid dispersions of nanoparticles. This astounding variety of applications of pgm materials is reflected in the current issue of Johnson Matthey Technology Review.

Vibrant Research

The production of pgm requires the extraction of pure pgm from multicomponent systems in which their content can vary considerably. Usually a multistep process is required to extract the different pgm in their pure form. Fedoseev et al. demonstrate the potential of hydrocarbonyl processes for the extraction of pgm from multicomponent chloride-sulfate solutions of industrial products, such as anode sludges generated during the extraction of cathode copper and nickel.

Metallic nanoparticles find a wide range of applications in sensors, catalysis, biomedical imaging, optochemical sensors, drug delivery systems and designing quantum dots. In most cases nanoparticles of pure metals are used. However, studies show that bimetallic nanoparticles (BMNP) show much higher catalytic capabilities. Therefore, BMNPs have become quite the hot topic for researchers and scientists across various spectra of interests. The work conducted by Kumar Verma et al. compares monometallic gold nanoparticles vs. gold/platinum BMNP. The influence of alloying on the thermal conductivity could have significant implications in various industrial applications.

Thin film coatings of pgm require bulk, high-purity metallic sputter targets. Ruthenium cannot be processed into sheet metal by conventional means due to its hexagonal crystal structure. Powder metallurgy technology is therefore required to produce fully dense substrates. The contribution of Zhang et al. demonstrates that the vacuum hot pressing of ruthenium powder can provide fine-grained blankets with mechanical properties close to electron-beam melted ruthenium.

Thermocouples are used by many of us in our daily work and we take it for granted that the correct temperature is shown. The mass loss of pgm under vacuum or air is well known, but studies that consider the actual effect of such evaporation on the accuracy of thermocouples are rare. The study presented in this issue showed that the mass loss in an actual thermocouple geometry was one order of magnitude lower compared to previous studies.

Unique Properties

Gas turbine engines expose construction materials to a combination of high temperature, highly reactive hot combustion gases, high static mechanical loads as well as low and high cycle fatigue. The standard materials for such applications are nickel and iron based superalloys. However, the need to improve turbine efficiency and to reduce CO₂ emissions requires an increase of the operation temperature. Platinum based superalloys have been discussed in the past as potential material for next generation turbines because they provide higher melting temperature and corrosion resistance compared to conventional superalloys. Hu et al. review the structural characteristics, mechanical properties,
oxidation resistance and corrosion behaviour of Pt-Al ternary, quaternary and multiple superalloys. Pt-Al-Cr-Ru alloys show the most promising properties and could be used up to a temperature 200 K higher than conventional superalloys.

While the high melting temperature of platinum is a benefit for high-temperature applications, some industries struggle with the challenges implied by the required processing temperatures. The investment casting of high quality and filigree jewellery items still remains a demanding task. Platinum based bulk metallic glasses that are reviewed by Houghton and Greer could provide new production opportunities. Their melting temperature is comparable to karat gold alloys. Above that, they offer the possibility for thermoplastic forming at very low temperature. Due to their very high hardness, they are supposed to offer greater wear resistance than conventional alloys. The research of platinum bulk metallic glasses offers much open land for further studies of this exciting class of material.

The current issue of *Johnson Matthey Technology Review* reflects the vibrant field of research on pgm based materials that ranges from nanoparticles to bulk materials. This is triggered by the unique properties of these materials that make them inevitable for many technological applications.

ULRICH E. KLOTZ
fem Research Institute Precious Metals + Metals Chemistry, 73525 Schwäbisch Gmünd, Germany
Email: klotz@fem-online.de
For the metals used in jewellery, high hardness and the associated scratch resistance are much sought after. Conventional crystalline alloys for jewellery are alloyed and extensively processed (thermally and mechanically) to improve hardness, but it is difficult to reach values beyond 300 HV. The advent of bulk metallic glasses (BMGs), based on precious metals and with hardness exceeding 300 HV in the as-cast state, is therefore of great interest for both jewellery and watchmaking. The non-crystalline structure of these materials not only gives high hardness, but also the opportunity to shape metals like plastics, via thermoplastic forming (TPF). For more traditional jewellery manufacture, BMGs also exhibit high-definition and near-net-shape casting. Gold-based alloys have long dominated the consideration of BMGs for jewellery as they can comply with 18 karat hallmarks. Although BMGs based on platinum or palladium possess excellent thermoplastic formability and are without known tarnishing problems, achieving useful glass-forming ability (GFA) within the more restrictive hallmarking standards typically used for jewellery (≥95 wt% platinum or palladium) is at best challenging. In this two-part review, platinum- and palladium-based BMGs are discussed, focusing on their potential application in jewellery and on the further research that is necessary.

1. Introduction

The metals conventionally used in jewellery are polycrystalline. Within each grain of these structures, the atoms are arranged in a regular periodic lattice. In metallic glasses (MGs), in contrast, there is no such long-range order: the atoms are densely packed in a solid state that has a liquid-like structure (1). Since they were first reported by Klement et al. in 1960 (2), MGs have been widely studied. Glass can be described as a hardened, cooled liquid.

The remarkably different structure of MGs leads to a set of unusual properties (Table I). Their high strength and hardness and a large elastic strain limit result in improved scratch and wear resistance. They also open up opportunities for novel intricate designs, making possible thinner and even hollow sections (6) and the use of hallmarked alloys in functional components of watches such as springs (11). The glassy structure also has many advantages for manufacture: near-net-shape casting with minimal casting defects and thermoplastic formability (12–14) are desirable for design innovation and economical mass production.

The ability to form a glassy state in metals was first observed on splat cooling an Au-Si eutectic alloy. Klement et al. produced partially glassy samples a few micrometres (<30 µm) thick (2). These samples were unstable but demonstrated that glassy metals form on rapid cooling (>10^6 K s⁻¹) of the liquid. Further research has led to the development of a range of glasses that can be cast with minimum dimension exceeding 1 mm. These are known as ‘bulk’ metallic glasses (BMGs). The first metallic glass with dimensions exceeding 1 mm was a
Further improvements came from melt fluxing that removes oxides (or other melt inclusions) that might promote crystallisation (16) (Section 1.1, Part II (17)). The most significant developments came in the early 1990s from separate research by Inoue et al. (18) and by Peker and Johnson (19).

In the years since, many glass-forming compositions have been identified in a wide range of systems including those based on the precious metals gold, silver, platinum and palladium (Figure 1) (14, 15, 28, 38). The critical cooling rate for glass formation \( R_c \), required to avoid crystallisation on cooling from the liquid, has generally been reduced, in some cases dramatically even to values below 100 K s\(^{-1}\). Consequently, BMGs can now be cast on the centimetre scale using a more extensive range of casting techniques. The same BMGs can also have excellent thermal stability, so a wide range of TPF techniques usually reserved for polymers and oxide glasses are now applicable (12–14).

The interest in BMGs for jewellery was sparked by Schroers et al.’s development of platinum- and gold-based BMGs that are compliant with 850Pt and 18 karat gold UK hallmarking standards (Table II) (4, 14, 28). The 950Pt, 950Pd, Sterling silver and gold hallmarks above 18 karat conflict with the alloying required for high GFA. Interest in intermediate hallmarks for palladium, such as ’585Pd’ (≥58.5 wt% palladium), exists but is not widespread (40). The compliance of gold-based BMGs with the much used 18 karat hallmark drew most attention (4, 41, 42). The majority of jewellery-related research has focused on their improvement, with a particular need to inhibit their abnormally fast tarnishing (3, 43–45). To date, silver-based systems have comparatively low GFA

---

**Table I: A Summary of the Advantageous and Disadvantageous Properties of Bulk Metallic Glasses and their Implications for Jewellery (3–10)**

<table>
<thead>
<tr>
<th>Properties</th>
<th>Implication for jewellery</th>
</tr>
</thead>
<tbody>
<tr>
<td>High yield stress</td>
<td>Better scratch and wear resistance</td>
</tr>
<tr>
<td>Minimal shrinkage on casting</td>
<td>Good surface definition</td>
</tr>
<tr>
<td>Thermoplastic formability</td>
<td>Economical scale of production</td>
</tr>
<tr>
<td>Lower casting temperature</td>
<td>Ease of production</td>
</tr>
<tr>
<td>Lower density</td>
<td>Smaller volume fills the same size mould (cost savings)</td>
</tr>
<tr>
<td>Four or more elements required</td>
<td>Difficulties in achieving high fineness</td>
</tr>
<tr>
<td>High viscosity and high</td>
<td>Issues with form filling</td>
</tr>
<tr>
<td>Deformation mode</td>
<td>Macroscopic brittle failure</td>
</tr>
</tbody>
</table>

---

**Fig. 1.** One measure of the ease of glass formation is the critical casting diameter \( d_c \), i.e. the diameter below which rod-shaped samples can be cast fully glassy. The optimum values obtained with different base metals cover a wide range. Data from (20–39)
and low silver contents (38); they are not suitable for jewellery.

The increase in popularity of platinum and palladium for jewellery means that developments in platinum- and palladium-based BMGs should not be ignored. Platinum has been widely used as a jewellery metal with varying popularity since the early 20th century. The metal has been used extensively by jewellers, including Carl Fabergé, for its lustrous appearance (46). A resurgence since the early 1960s and the introduction of platinum hallmarking standards in 1975 means that today around 26% of all platinum consumption is for use in jewellery (47). Palladium is becoming an ever more popular choice since the introduction of hallmarking standards in 2010.

Platinum, palladium and gold are face-centred cubic (fcc) metals that, when pure, are so soft (hardness below 75 HV) as to be practically useless. Consequently, it is standard practice to alloy them with other metals such as copper, silver, ruthenium, rhodium, iridium, cobalt, chromium, gallium and indium (8, 40, 48–53). The limited alloying achievable within high fineness hallmarks or stamping regulations outside the UK (Table II) means most alloys are solid solutions. They therefore require extensive thermomechanical treatments to achieve desirable hardness (40, 48). A final hardness of 150–200 HV is typical (8). Minimum requirements for jewellery and watchmaking are 100 HV and 300 HV, respectively (8).

Even extensive thermomechanical treatments of two-phase platinum alloys fail to achieve hardness values surpassing 300 HV (48). There is a clear need for alternative routes to hallmark-compliant platinum and palladium alloys with high hardness and improved scratch resistance. Furthermore, platinum and palladium have high melting points requiring casting temperatures over 2000 K (approx. 1750°C) (11, 28). Such high temperatures introduce many problems for jewellery casting such as reactions with the crucible, tarnishing and oxidation at high temperature and shrinkage-related defects (28).

As discussed in this review, hallmark-compliant BMGs offer a solution to many of the problems currently facing precious-metal jewellery alloys (Table I), but the alloying requirements for GFA and hallmark compliance are mostly opposing and therefore present a significant challenge. Following a brief introduction to the science of MGs, platinum- and palladium-based BMGs suitable for jewellery are discussed, alongside their desirable mechanical properties, processability and corrosion resistance.

2. Bulk Metallic Glasses: A Brief Explanation

MGs are formed when the molten liquid is cooled fast enough to avoid crystallisation. On cooling, the liquid becomes more and more viscous and below the glass-transition temperature \( T_g \) the atoms undergo substantial thermal arrest; they are ‘frozen’ into a liquid-like arrangement, so crystallisation cannot readily occur. The glass transition is a kinetic phenomenon, not a thermodynamic one. Compared with conventional oxide glasses and polymers, the viscosity of metallic liquids is low, associated with the isotropic non-directional nature of metallic bonding (54). Correspondingly, MGs have comparatively high \( R_c \).

Despite having no long-range order, the structure of MGs shows substantial short-range order (SRO) and medium-range order (MRO). The structure of the liquid and the subsequent MG can be considered
in terms of stable atom-centred clusters that reduce mobility and inhibit atomic rearrangement that would lead to crystallisation. The liquid viscosity $\eta$ decreases rapidly with increasing temperature just above $T_g$ (Figure 2). This decrease is described by the kinetic ‘fragility’, a term that refers to the progressive breakdown of order in the liquid as it is heated and not to a mechanical property. One parameter used to characterise the fragility is $m$ (58), Equation (i):

$$
m = \left(\frac{d \log (\eta)}{dT}\right)_{T = T_g}
$$

Liquids with low $m$ are termed ‘strong’ and those with high $m$ are termed ‘fragile’. While the liquids from which MGs are formed are all ‘fragile’ compared with the liquids giving conventional oxide glasses (i.e. their viscosity is more sensitive to temperature above $T_g$), their carefully chosen compositions make them ‘strong’ compared to pure-metal melts or to the liquids from which typical crystalline engineering alloys are cast.

Even so, there is a significant range of $m$-fragility amongst those liquids that form MGs. Those liquids with high $m$ (‘stronger’ liquids) have viscosities that decrease less on heating above $T_g$. Compared to other liquids at the same $T/T_g$, these liquids have a higher viscosity and therefore lower atomic mobility. Atoms in a ‘stronger’ liquid are less able to rearrange and in the absence of other factors, such liquids should be better glass formers (61, 62). Characteristics favouring high GFA have been summarised by Inoue as ‘empirical rules’ (57), which have led to the development of BMGs with $R_c$ well below 100 K s$^{-1}$ and the casting of glassy products on the centimetre scale (63).

Even when a MG can be made, it is difficult to determine $R_c$ and the associated $d_c$ with precision. In any case, in trying to develop new compositions, it would be preferable to have a guide to GFA based on parameters derived only from thermophysical data. Several parameters have been suggested, reflecting the thermodynamics and kinetics involved in glass formation, and these can show a good correlation with $R_c$ (63).

The reduced glass-transition temperature $T_{rg}$ is defined by Equation (ii):

$$
T_{rg} = \frac{T_g}{T_L}
$$

Turnbull proposed that a high value of $T_{rg}$, more specifically $> 2/3$, would indicate a good glass-forming composition (1). A high $T_{rg}$ means a small interval between $T_L$ and $T_g$ (Figure 3). This minimises the temperature interval in which crystallisation is possible both thermodynamically and kinetically. While it is possible to raise $T_g$, the glass transition remains poorly understood. The compositional variation of $T_g$ is comparatively weak, however, so the variation of $T_L$ is critical. Eutectic or near-eutectic compositions have strongly suppressed $T_L$ and so remain the preferred, but not the only, choice for high-GFA alloys (38). As will be discussed, the composition of these low-lying eutectics, typically in the range 20–30 at% metalloid, is problematic for high fineness BMGs.

Fig. 2. An Angell plot (58) showing the variation in viscosity with temperature above $T_g$. Orthoterpheynyl, silica and conventional window glass are shown for comparison with several platinum- and palladium-based BMGs and a so-called ‘benchmark glass-former’ zirconium-based BMG. Data obtained from (59, 60)
Once formed, the glassy structure remains metastable. On heating, the atomic mobility increases. Once the temperature exceeds \( \sim 0.6 T_g \), relaxation occurs (i.e. changes in the glassy structure that do not involve crystallisation or phase separation). First, there are local atomic rearrangements, known as \( \beta \) relaxation (64). These occur in a chain-like manner and lead to short-range chemical ordering (9, 65). Near \( T_g \), global and coordinated rearrangements may occur, known as \( \alpha \) relaxation (64), which allow the transition from glass into the supercooled liquid state. Ultimately, the supercooled liquid will crystallise into the equilibrium crystalline phases.

On heating in calorimetry, crystallisation shows its onset at \( T_x \) (Figure 4). Like \( T_g \), \( T_x \) is kinetically controlled and is, therefore, a function of the heating rate (66). As a sample is heated at a higher rate, the transitions to the liquid and to the crystalline states must occur faster, therefore at higher temperature: the measured values of \( T_g \) and \( T_x \) are higher. The region bounded by \( T_g \) and \( T_x \) is the supercooled liquid region (SCLR) and is characterised by \( \Delta T_x \), Equation (iii):

\[
\Delta T = T_x - T_g \tag{iii}
\]

The SCLR is important as the region relevant for TPF (12, 13). The width of the SCLR, \( \Delta T_x \), also indicates the stability of the supercooled liquid. Inoue proposes that an excellent glass-forming system has a high \( T_{rg} \) (for high GFA) and a wide \( \Delta T_x \) (for excellent thermal stability) (67).
In the SCLR, the metastable supercooled liquid can undergo homogeneous viscous flow, reaching strains of several hundred percent (13, 68–70). After some time of holding in the SCLR, crystallisation begins and ultimately proceeds to completion. A wider SCLR (greater \( \Delta T_x \)) indicates greater resistance to crystallisation and improves the thermoplastic formability of the MG (14). For best correlation with thermoplastic formability, Schroers argues that \( \Delta T_x \) should to be normalised by \( (T_L - T_g) \) (12, 14). A large \( \Delta T_x/(T_L - T_g) \) means a larger viscosity change within the SCLR, allowing greater deformation during TPF. The \( S \) parameter, Equation (iv):

\[
S = \frac{\Delta T_x}{T_L - T_g}
\]  

(\text{iv})

although omitting the effect of liquid fragility (Figure 2), correlates remarkably well with thermoplastic formability, making it an effective tool for comparison of different glass compositions (12, 71). While thermoplastic formability shows even better correlation with other parameters (for example, constant heating formability \( P^\text{scan} \) (13, 71)), \( S \) has the advantage that it can be calculated from a single calorimetric experiment (Figure 4), so is more readily adopted as a simple guide. In this review, \( T_{rg}, \Delta T_x \) and \( S \) are used to compare GFA and thermoplastic formability.

3. Glass-Forming Ability of Platinum-and Palladium-Based Bulk Metallic Glasses

The remarkable properties of platinum-based and palladium-based BMGs and the particularly high GFA of palladium-based compositions (Figure 1) means they have been the subject of substantial research. While being initially developed for scratch-resistant, hallmark-compliant jewellery, it was found that some platinum-based BMGs show a record-breaking combination of excellent strength and toughness (72–74).

3.1 Platinum-Phosphorus and Palladium-Phosphorus Based Systems

Metal-metalloid alloy systems can be excellent glass-formers. This is attributed to the small metalloid atoms occupying interstitial sites between the dense-random-packed metal atoms. The strong bonding between metal and metalloid atoms further helps to give a stable dense packing (75). Pt-P and Pd-P binary eutectics are popular starting points for BMGs with further alloying additions, such as nickel and copper, leading to a substantial increase in GFA (76–78). From a topological standpoint, these additions help to form efficiently packed clusters. As proposed by Miracle et al., the form of these clusters depends on the relative sizes of the constituent atoms (79–82).

Following the discovery of palladium-based bulk glass formers by Chen and Turnbull (15), the Pd-Ni-P ternary eutectic has received particular attention. Partial substitution of nickel with copper leads to a dramatic rise in GFA. The heats of mixing for Pd-Cu, Ni-Cu and Cu-P pairs are more strongly negative than for Pd-Ni (76) and lead to a change in the dense packing of atoms in the viscous liquid (77). Further refinements in composition resulted in an alloy with \( d_C \) on centimetre scale and wide \( \Delta T_x \) (83). The maximum GFA was later attributed to having the same chemical SRO of nickel and copper around phosphorus (78). These BMGs are particularly stable against crystallisation (84–88). When crystallisation eventually occurs in the SCLR, several ordered and complex crystalline phases are formed in a single cooperative transformation. The excellent GFA is attributed to the difficulty of crystallising the ordered Pd\(_x\)Cu phase. Compared to other BMGs, the nose of the crystallisation curve on the time-temperature-transformation (TTT) diagram (the temperature at which crystallisation is fastest) for Pd\(_{60}\)Ni\(_{10}\)Cu\(_{30}\)P\(_{20}\) lies at a time 10 times longer than for the benchmark glass-former Vitreloy\(_\text{TM} \)\(_1\) (85, 89). The time before crystallisation onset is, however, still short: for a Pd\(_{43}\)Ni\(_{16}\)Cu\(_{22}\)P\(_{22}\) sample held just above \( T_g \) this is \( 10^4 \) s (84, 89). Below \( T_g \), times to the onset of crystallisation are orders of magnitude longer due to the dramatically lower atomic mobility.

While palladium-based BMGs have been studied since the 1970s, platinum-based BMGs are a comparatively recent development. In 2004, Schroers and Johnson reported two novel platinum-based BMG compositions, Pt\(_{57.5}\)Cu\(_{14.7}\)Ni\(_{16.3}\)P\(_{22.5}\) and Pt\(_{60}\)Cu\(_{16}\)Co\(_{8}\)P\(_{22}\) (28). These show high GFA when their melts are fluxed with B\(_2\)O\(_3\) (\( d_C > 10 \) mm), good thermal stability (\( \Delta T_x > 60 \) K), exceptional thermoplastic formability (\( S > 0.20 \)), as well as being processable in air (28) (which is difficult for zirconium-based BMGs, for example).

For jewellery, Pt\(_{60}\)Cu\(_{16}\)Co\(_{8}\)P\(_{22}\) is particularly attractive due to its high platinum content (satisfying the 850Pt hallmark) and the absence of skin-sensitising nickel (28, 41, 42, 45). On the
other hand, Pt$_{57.5}$Cu$_{14.7}$Ni$_{5.3}$P$_{22.5}$ attracted much attention from researchers. Its plastic strain of 20% and fracture toughness of 80 MPa m$^{1/2}$ far exceed any previously reported values for BMGs (28, 72). Further studies have reported fracture toughness for both palladium- and platinum-rich BMGs as high as 200 MPa m$^{1/2}$ (73, 74) — a value comparable to many low-carbon steels widely used as structural materials.

This unique combination of high hardness and high plasticity has been linked to their high Poisson ratio (>0.4) in the glassy state, which itself is related to high m-fragility in the liquid state (72–74). High Poisson ratio corresponds to a low ratio of shear modulus G to bulk modulus B. The low value of G/B indicates that resistance to shear (proportional to G) is low compared to resistance to cavitation (proportional to B). While a typical BMG would fail by the operation of a single dominant shear band, leading to macroscopic plasticity below 1%, these BMGs flow by the operation of multiple shear bands leading to high macroscopic plasticity (72).

While high m-fragility of the glass-forming liquid is associated with desirable fracture toughness, it is also associated with reduced GFA (62, 87). The exceptional GFA of both Pt-P and Pd-P based BMGs is therefore surprising (72–74, 76, 77, 90, 91). As noted above, high GFA is typically associated with strong liquids (62). Fragile liquids do not aid glass formation through high viscosity (low atomic mobility), but high GFA may result also from a low thermodynamic driving force for crystallisation, or a high crystal-liquid interfacial energy (inhibiting crystal nucleation) (87, 92). Studies report that a low driving force for crystallisation stabilises Pd$_{43}$Cu$_{27}$Ni$_{10}$P$_{20}$ while high interfacial energy stabilises Pt$_{57.5}$Cu$_{14.7}$Ni$_{5.3}$P$_{22.5}$ (87). The nature of stabilisation helps to explain why fluxing has such a pronounced effect on the GFA of these alloys, since the presence of any heterogeneous nucleation sites, notably oxide inclusions, substantially lowers their resistance to crystallisation.

Measurement of crystallisation kinetics over the full temperature range from $T_L$ down to $T_g$ is helpful in understanding the mechanisms. A classical TTT diagram shows the times necessary for the progress of crystallisation in the supercooled liquid upon isothermal holding at each temperature. The times, for example for crystallisation onset, follow a C-curve in which the minimum time (at the nose of the curve) lies between $T_L$ and $T_g$. At higher temperature than the nose, the kinetics is controlled by crystal nucleation, and at lower temperature by crystal growth. In most cases, for example, for a zirconium-based BMG-forming alloy, the C-curve is asymmetric with the temperature of the nose much closer to $T_L$ than to $T_g$ (62).

In contrast, the C-curves for palladium- and platinum-based alloys are more symmetric (84, 87, 91). For Pd$_{43}$Ni$_{10}$Cu$_{27}$P$_{20}$ (89), for example, the nose lies roughly halfway between $T_L$ and $T_g$. As the m-fragility of palladium-based BMG-forming liquids is relatively high ($m$>50 (93)), the kinetics nearer to $T_L$ should be relatively accelerated, which, in the absence of other factors would impart greater asymmetry to the C-curve. The special feature of Pd$_{43}$Ni$_{10}$Cu$_{27}$P$_{20}$, and palladium- and platinum-based BMG-forming compositions in general, is thus identified as difficulty in crystal nucleation (89). Indeed, the nucleation is mostly possible only because of the influence of heterogeneities (89). This explains why fluxing (which can remove heterogeneous nucleation sites, notably oxide inclusions, Section 1.1, Part II (17)) can dramatically improve the GFA of these alloys.

Recent work on the structures of Pd-P and Pt-P based BMGs provides insight into the critical features required for high GFA (92, 94–97). Detailed studies show that the crystal-liquid interfacial energy in Pt-Cu-(Ni/Co)-P BMGs is three times that in kinetically stabilised zirconium-based BMGs (94). The dramatic improvement in GFA with overheating above $T_L$ to dissolve all preexisting structures in the liquid, provides further evidence that these glasses are stabilised by the barrier to crystal nucleation (94, 96).

In the search for BMGs with high weight fractions of platinum or palladium, understanding the liquid kinetics is imperative. Studies suggest that Pt-P based liquids with higher platinum content are more fragile (95, 97). This is relevant, given the desire in jewellery for platinum contents exceeding 95 wt% (approx. 70 at%). In Pd-(Cu,Ni)-P BMGs, increasing m-fragility with higher palladium contents is attributed to the less pronounced bifurcation into Pd-Cu-P and Pd-Ni-P clusters with different coordination shells around the central phosphorus atom (77, 95, 97). These two structural units were suggested to develop MRO that stabilises the supercooled liquid and is responsible for the stronger liquid behaviour (95). Topological-based assumptions that Pd-P and Pt-P liquids have similar structures led to the expectation that the same structural changes would occur in Pt-P liquids (95). In practice, the liquids show substantial differences in SRO and MRO (97, 98). While icosahedral SRO dominates in Pd-P liquids, Pt-P liquids contain many more trigonal prismatic
structural units, leading to the observation of pronounced MRO. This MRO is not observed at high temperatures, unlike the icosahedral SRO in Pd-P liquids, resulting in more pronounced ordering during cooling towards \( T_g \) (95, 97). As a result, Pt-P liquids have a much broader distribution of cluster connection schemes, comprising the more flexible two- and four-atom connections, whereas the stiffer three-atom connections prevail in the Pt-P-based liquids (97). The presence of SRO at high temperatures and a relative lack of ordering on the medium length-scale in Pt-P-based liquids lead to a low entropy of fusion compared with Pt-P-based liquids. This explains the low driving force for crystallisation in Pt-P-based liquids (62, 83, 87, 98, 99) as well as the more pronounced sensitivity of plasticity to the cooling rate during glass formation (97, 100, 101). Regardless of the differences when compared with Pt-P-based liquids, the high m-fragility of Pt-P-based liquids does mean that there is still substantial ordering on cooling towards \( T_g \); fragility is dependent on the rate of ordering near \( T_g \), not on the type of ordering (92).

### 3.2 Bulk Metallic Glasses for Jewellery

The primary restriction on BMGs for jewellery is hallmarking standards (as practised in the UK) and stamping regulations (US equivalent). These hallmarking standards place a minimum weight fraction on platinum, palladium, gold and silver to guarantee quality (Table II). Of these hallmarks, 18 karat gold, 950Pt, 900Pt, 950Pd and sterling silver are predominantly used for jewellery.

Alongside the requirement for a minimum weight fraction of precious metal, jewellery alloys must also be without skin-sensitising elements such as nickel (42, 45, 102). Consequently, many of the otherwise attractive glass-forming compositions are unsuitable for jewellery. Although studies suggest that the ion release rate of nickel from glassy alloys is well below the legal requirement (45), there is an industry-wide desire to eliminate such elements (103). Nickel-free BMGs are also of substantial interest for dental and biomedical applications (104, 105).

Schroers and Johnson’s discovery of 850Pt BMGs was, therefore, a breakthrough (28). The high GFA, high m-fragility and low \( T_g \) of these liquids are desirable for high-definition TPF (41, 71, 106). Low casting temperatures and the glassy structure itself appear to solve many issues in jewellery manufacture (Section 1, Part II (17)), while the unique properties of BMGs can be exploited for scratch-resistance and other property enhancements (Section 2, Part II (17)). Still, it is the high 950Pt and 950Pd hallmarks that are the most desirable for jewellery. Given the inevitably high capital cost that would be associated with the manufacture of BMGs using techniques that are novel and unfamiliar to goldsmiths, BMG jewellery would, at least initially, be expensive. Hence 950Pt and 950Pd hallmark-compliant BMGs would be desirable, if not, essential. It is conceivable that the majority of consumers would justify the cost of these materials by fineness alone. While the 900Pt hallmark is widely used by jewellers and offers a wider ‘compositional space’ for alloy development, it would not command as high a price.

Attempting to achieve such high-fineness hallmarks heavily restricts the extent of alloying, and yet, as discussed above, alloying is necessary to achieve high GFA. The platinum-rich (95 wt% platinum) and palladium-rich BMGs (90 wt% palladium) developed by Demetriou et al. (73, 74) are, therefore, both scientifically and industrially significant. Through microalloying (i.e. minor additions of elements), they were able to achieve high weight fractions of platinum and palladium in fully glassy samples, albeit with relatively poor GFA. While Demetriou et al. are correct that their 950Pt BMG would be suitable for jewellery (73), this risks ignoring practical issues. Techniques such as tilt casting, suitable for industrial jewellery manufacture, cannot achieve the cooling rates achieved by expensive, small-scale, laboratory techniques such as suction casting. In an industrial environment, it will be challenging to cast these alloys into a fully glassy state. Furthermore, jewellery alloys often contain a higher fraction of precious metal than hallmark requirements stipulate. This tolerance ensures that all items produced are hallmark-compliant. Increasing the weight fraction of platinum or palladium any further in these alloys is likely to result in the loss of useful GFA.

The work of Demetriou et al. (73, 74) shows that, with difficulty, 950Pt and high fineness palladium (90 wt%) hallmark-compliant BMGs are achievable, but the best alloys developed so far are still relatively poor bulk glass formers. The necessity to add more than approximately 15 at% metalloids to achieve high GFA means that achieving high fineness is difficult.

Microalloying may be key in achieving better compositions, although its effects are poorly
understood. Minor additions can have a significant impact on GFA: adding 0.3 at% silver to Pt74.7Cu1.5P10.8B2.5Si1.5 increases $d_c$ by a factor of two, albeit from a low level (73). Additions of up to 2 at% gold or silver increase GFA in Pd79Cu32Si10P5 (86), rationalised using a topological argument (although joint additions yield less impressive results).

The effect of microalloying on properties of BMGs appears specific to the added element (107, 108), suggesting that both chemical and topological effects are important. From a topological viewpoint, microalloying is expected to increase the variety of local atomic configurations (108–110). This may affect local atomic rearrangements ($\beta$ relaxation) linked to spatial heterogeneity (111) and therefore the properties of BMGs below $T_g$. Faster $\beta$ relaxation due to microalloying (109) is expected to significantly affect a wide range of properties, from corrosion and tarnishing behaviour (65, 112) to sub-$T_g$ embrittlement (97, 112–115). If microalloying is to be employed in platinum- and palladium-based systems to permit an increase in the precious-metal weight fraction, a deeper understanding is required of its effect on glass properties and GFA.

### 3.3 Phosphorus-Free Bulk Metallic Glasses

Alloys containing phosphorus are challenging to process. Its reactivity means additional processing steps, such as prealloying, are required (11). Pt-P and Pd-P binary eutectics are, therefore, not ideal starting points for glassy jewellery alloys (11).

For platinum-based BMGs, extensive work by Kazemi et al. has identified the Pt-Si-B ternary eutectic as a suitable starting point (11) for alloy development. The eutectic composition lies at a high atomic percentage of platinum, while the weight percentage of platinum is aided by the low atomic masses of silicon and boron. Many other M-Si-B eutectics (M = nickel, cobalt, iron) have high GFA, which is rationalised by topological arguments (67, 116, 117). Prior studies, comparing the GFA of Pd-Si and Pd-Si-B, further support expectations of a high-GFA platinum-based BMG (118). By substituting copper for platinum, and germanium for silicon, at the Pt-Si-B ternary eutectic composition, a Pt-Cu-B-Si-Ge BMG with a 5 mm was developed (11).

In contrast to phosphorus-containing BMGs, Kazemi et al.’s Pt49.95Cu16.65Si6.4Ge3.B24 alloy is unaffected by fluxing. Prolonged fluxing with $B_2O_3$

did not reduce the oxygen content (119). While oxygen-scavenging by alloying with scandium was successful in reducing oxygen content, the GFA was not improved (119). Instead, all GFA was lost when more than 2 at% scandium was substituted for copper (119). Scandium and holmium additions were found to sharply increase $T_g$ and $T_m$ with a concomitant rise in hardness. These additions also led to a rise in $T_g$, ultimately leading to a loss of GFA (lower $T_m$) (119). While oxygen scavenging, minor additions of large-atomic-radius rare-earth metals and prolonged fluxing all improve the GFA of Pt-P (87, 120, 121), their failure to do so for Pt-Si-B suggests that the controlling factors are different. To elucidate these and to optimise alloy compositions, it would be helpful to know the fragility of the liquid: no values have been reported, but the liquid is expected to be relatively fragile.

Apart from Pd-P, only the Pd-Si eutectic has been reported as a suitable starting point for BMGs. Early work by Chen and Turnbull focused on the Pd-Cu-Si ternary eutectic, yielding high-GFA alloys (15). The similarity in weight fraction of palladium between Pd-P and Pd-Si means, as for platinum-based BMGs, that high fineness and high GFA conflict with one another. Many Pd-Si-based glass formers have low weight fractions of palladium and are therefore not suitable for jewellery. They have, however, attracted much interest for their use as biomedical and dental materials due to their high plasticity, absence of skin-sensitising elements and excellent corrosion resistance (104, 105).

Although high fineness is still challenging, the Pd-Si binary eutectic serves as an excellent starting point for BMGs. Pd-Si binary alloys are remarkably good glass formers; the glasses exhibit high activation energies for crystallisation (122), resulting in high thermal stability. However, only after a careful choice of elements with low atomic mass and suitable atomic radii is the suggestion of a 950Pd hallmark-compliant BMG plausible.

Reports of Pd79Au1.5Ag3Si16.5 ($d_c = 3$ mm) (105) and Pd75Si15Ag3Cu2 ($d_c = 10$ mm) (123) BMGs support these claims. These are two of the highest fineness phosphorus-free palladium-based BMGs reported so far, with weight fractions around 90 wt% palladium before further alloying. Pd75Si15Ag3Cu2 is also readily formed using TPF and does not require $B_2O_3$ fluxing, making it easier to manufacture (123). While a phosphorus-free BMG would be desirable, small additions of phosphorus can improve GFA and permit an increased weight fraction of palladium (124).
Further research on 950Pt and 950Pd hallmark-compliant BMGs with a GFA suitable for industrial manufacture is challenging. The inevitable high $m$-fragility of these alloys means that high cooling rates and carefully optimised processing are likely to be requirements. Research has mostly focussed on Pt-(Cu, Ni)-P and Pd-(Cu, Ni)-P based BMGs (16, 20, 41, 42, 73, 74, 84, 89, 90, 104, 125) with some interest shown in Pt-Si-B and Pd-Cu-Si based BMGs (85, 86, 88, 105, 123, 124).

Further optimisation through careful alloying and microalloying may help to identify additional 950Pt BMGs and novel 950Pd BMGs with sufficient GFA. While other systems such as Pd-Ni-S BMGs or novel high-entropy BMGs exist, they have low palladium contents and so do not seem suitable for jewellery (5, 126). Li et al. suggest that there may exist up to $10^6$ BMG compositions (127), so the search for new glass-forming compositions should continue. New combinatorial techniques to assess $\Delta T_k$ and $T_{rg}$ (128–130), and computational techniques (131–133), allow more efficient sampling of compositional space for undiscovered high GFA compositions. A new search with these techniques may yield results that cannot readily be predicted and rationalised using empirical rules and experimentally determined phase diagrams.

References

23. T. Zhang, R. Li and S. Pang, *J. Alloys Compd.*, 2009, **483**, (1–2), 60
70. F. Spaepen, *Scr. Mater.*, 2006, **54**, (3), 363
90. N. Nishiyama and A. Inoue, Mater. Trans., JIM, 1996, 37, (10), 1531
100. G. Kumar, S. Prades-Rodel, A. Blatter and J. Schroers, Scr. Mater., 2011, 65, (7), 585
120. Z. P. Lu and C. T. Liu, J. Mater. Sci., 2004, 39, 3965
122. N. Chen, Y. Li and K.-F. Yao, J. Alloys Compd., 2010, 504, (S1), S211
124. L. Liu, A. Inoue and T. Zhang, Mater. Trans., 2005, 46, (2), 376


### The Authors

Owain Houghton is a PhD student at the University of Cambridge, UK. He obtained a BA degree in Natural Sciences and an MSci degree in Materials Science from the same institution. He researches bulk metallic glasses based on precious metals and their potential applications for jewellery as a member of the Microstructural Kinetics Group.

A. Lindsay Greer is a professor of Materials Science at the University of Cambridge. He received MA and PhD degrees from Cambridge and holds Honorary Doctorates from AGH University of Science and Technology, Cracow, Poland, and the University of Sofia, Bulgaria. He was an assistant professor at Harvard University, USA; has held visiting positions in Grenoble, France; St. Louis, USA; Vienna, Austria; and Turin, Italy; and is a foreign principal investigator in the Advanced Institute for Materials Research, Tohoku University, Japan. He leads the Microstructural Kinetics Group, and his current research focuses mainly on metallic glasses. He is a coauthor of some 450 papers.
A Conflict of Fineness and Stability: Platinum- and Palladium-Based Bulk Metallic Glasses for Jewellery: Part II

Processing, tarnish resistance and future developments

O. S. Houghton*, A. L. Greer
Department of Materials Science and Metallurgy, University of Cambridge, 27 Charles Babbage Road, Cambridge, CB3 0FS, UK
*Email: osh24@cam.ac.uk

The properties and glass-forming ability (GFA) of platinum- and palladium-based bulk metallic glasses (BMGs) for jewellery were introduced in Part I of this two-part review (1). Here, we will describe methods for their processing, tarnishing and corrosion resistance and consider their prospects and future developments.

1. Processing: Injection Moulding Meets Metals

1.1 Fluxing and Melt Contamination

The initial report (2) of fluxing of liquid Pd$_{40}$Ni$_{40}$P$_{20}$ with anhydrous liquid B$_2$O$_3$ showed that this treatment facilitates reliable production of fully glassy samples with larger cross-section. Although other agents such as soda-lime glass (3) have been used, B$_2$O$_3$ has remained the flux of choice for palladium-based and, later, platinum-based systems (4–15). While fluxing is an additional processing step, it is used because the effects can be dramatic: it can improve GFA, characterised as a reduction in $R_c$, by one or more orders of magnitude (6, 11, 16, 17). In a Pd-(Cu,Ni)-P BMG, fluxing increases the onset time at the nose of the time-temperature-transformation (TTT) curve for crystallisation in the liquid from 130 s to 200 s (17) and has been critical in achieving BMG castings over 50 mm in minimum linear dimension (18, 19).

Fluxing works by reducing the influence of heterogeneous nucleants that would facilitate crystallisation on cooling the melt. These nucleants are generally considered to be dispersed particles, mostly oxides, in the melt, but fluxing may also prevent contact with nucleants at the melt surface. Fluxing works by preferential wetting of the particles, possibly followed by dissolution of the particles in the flux. The removal of oxide particles from the melt would reduce its oxygen content. Direct verification of this is rare but, in one study, an initial oxygen content of ~12 ppm (by weight) was reduced to ~5 ppm by fluxing (8). Following the initial work (2), it is usual to cycle the melt between solid and liquid states several times; crystallisation in early cycles may assist in driving inclusions to the surface of the alloy, facilitating their take-up by the flux.

Ideally, fluxing would have no effect on the composition of the liquid alloy itself. In particular, when using B$_2$O$_3$, none of the elements in the alloy should have a greater ‘oxygen affinity’ (11), i.e. more stable oxide (as quantified by the relevant chemical potentials), than the boron in the flux. Alloys of the systems Pd-(Cu,Ni)-P and Pt-(Cu,Ni)-P meet this condition. But B$_2$O$_3$ has also been used to flux Pd-Cu-Si (8): in this case, reaction with silicon in the alloy can reduce B$_2$O$_3$, leading to dissolution of boron into the alloy. The addition of boron is detrimental to the GFA and the overall effects of fluxing are therefore complex, varying markedly with the time-temperature profile used in the treatment (8, 11). Nevertheless, by optimising the fluxing of Pd-Cu-Si, its $d_c$ can be substantially improved to 11 mm (20) and 15 mm (8). Studies
of Pd-Ni-Si-P alloys suggest that composition changes inducing by fluxing with B₂O₃ can in some cases be beneficial for GFA (7, 17, 21) and lead to improvements in plasticity (22).

The remarkable improvements in GFA for ternary BMGs suggest that the fluxing should be considered in greater detail. The high m-fragility of, and the boron content within, Demetriou et al.'s 950Pt based BMG suggests a sensitivity to fluxing and boron pick-up (23), so enhanced fluxing procedures should be sought. Perhaps the effects of fluxing and overheating (to dissolve preexisting structures in the melt) should be revisited for alloys where it has been previously reported that fluxing does not affect GFA. It would be good to explore the use of alternative fluxes. B₂O₃ has been very widely used, not least because it remains liquid below the Tₘ of the alloys being processed. It may be possible to find multicomponent fluxes that remain liquid to similar temperatures, yet have greater resistance to chemical reduction by reaction with the alloy being processed.

In the literature, the action of fluxing has been described as 'purification' of the liquid alloy. While fluxing may clean an alloy by removing dispersed particles, there is no evidence that it can reduce levels of dissolved impurities. In contrast, as noted above, the alloy can be contaminated by reaction with the flux. In the production of BMGs, impurities can be detrimental to GFA. The most prominent example is the presence of oxygen in zirconium-based alloys, as briefly reviewed elsewhere (11). It is important to start with raw materials of ultra-low oxygen content and care must always be taken to minimise oxygen pick-up during processing. Various approaches have been adopted to reduce the oxygen content; these include oxygen scavenging with low addition levels of elements such as yttrium and scandium (24). In addition to the scavenging effect, these elements with large atomic diameter are likely to have microalloying effects that improve the GFA (24).

For palladium- and platinum-based glass-forming alloys, in contrast, there is little concern about oxygen as a dissolved impurity. Nevertheless, it remains desirable (in some cases essential) to use raw materials of high purity and to minimise pick-up of impurities during processing.

### 1.2 Direct Casting

In conventional investment casting of platinum alloys, their high Tₘ (around 2000 K) limits the casting size (25) and introduces many issues such as reactions with the crucible, tarnishing and oxidation, plus significant casting shrinkage and porosity (as high as 5%) (26). While palladium jewellery alloys are cast at slightly lower temperatures (27), the further reductions in casting temperatures offered by BMG-forming compositions are still desirable. The low-lying eutectics of platinum-based and palladium-based BMGs offer an exciting opportunity for easier processing of precious-metal jewellery alloys.

The main challenges in casting BMGs arise from the high cooling rates required to avoid crystallisation and the high viscosity of the glass-forming liquid compared with the melts of usual crystalline alloys. In conventional casting techniques, good form-filling requires long casting times (i.e. slow filling), which are longer for more viscous liquids. For glass formation, techniques with low cooling rates (for example, investment casting), are not suitable or need adapting. In any case, the casting size is limited by dₘ. The undesirability of cold-working BMGs (due to possible fracture or the formation of unsightly surface steps) requires items to be cast near to their final shape.

Nevertheless, for direct conventional casting, BMGs present many advantages when compared with conventional crystalline alloys and this remains a practical processing route for jewellery. The absence of a first-order phase transition on cooling to form a glass means that there is no substantial shrinkage during casting. Even if any crystallisation were to occur, these glass-forming liquids exhibit small crystallisation shrinkages (28).

Casting porosity is a particular problem for many platinum jewellery alloys (26), motivating the introduction of hot isostatic pressing of castings. In palladium-based jewellery, 950Pd alloys suitable for high-quality investment casting are the focus of active research and development (29). For BMGs, low volume shrinkage (< 0.5%) on casting means near-net-shape casting can be achieved with few casting defects such as porosity and with high surface definition. Their lower casting temperatures also lead to lower thermal stresses during cooling to ambient temperature (30). Fewer polishing steps are required after casting due to the absence of crystallinity; ultimately, there can be an atomically smooth surface finish (31).

Unlike zirconium-based BMGs, which are already used in luxury goods markets (32), BMGs based on precious metals (gold, palladium and platinum) for jewellery have the considerable advantage of being processable in air (4, 30, 33–36).
The casting of gold-based BMGs for jewellery has been evaluated in detail (37–39). Similar information for platinum- and palladium-based BMGs is not as readily available, but their comparably high fragilities and larger $d_c$ values (Table I) mean that their castability is similar, if not better. The only significant difference is the requirement to flux with $\text{B}_2\text{O}_3$ before casting. BMGs based on precious metals perform well compared with so-called ‘benchmark’ BMGs which have exceptional processability (32, 34).

Many BMGs can be made using methods such as tilt casting, suction casting and centrifugal casting. While methods such as suction-casting achieve higher cooling rates and higher-quality castings with low porosity (44), die-casting and tilt-casting techniques are scalable to high-volume production (45). High flow rates can induce crystallisation throughout the sample due to shear thinning of the liquid and should be avoided (46). As a result, methods such as centrifugal casting and continuous casting are difficult to apply to BMGs (38, 47, 48). Some heterogeneous nucleation of crystals is inevitable in contact with the copper mould (49).

For BMGs as a jewellery material, tilt-casting appears the most suitable conventional method. Although maximum cooling rates and form-filling are lower than for suction-casting, the method is suitable for industry and has been successfully used to cast samples in massive copper moulds in many of the studies presented here.

For the most intricate designs, a goldsmith uses investment casting. In this method, high form-filling is achieved by slow cooling. While slow cooling gives enough time for the melt to fill the entire mould (37), it is incompatible with the requirements for glass formation. To circumvent this problem, Eisenbart et al. developed a lost-metal mould casting technique, which is an analogue to investment casting for BMGs (39). In their technique, a wax pattern is produced and covered in a thin layer of conducting material. Electroforming is then used to deposit copper onto the wax pattern. The mass of copper deposited is typically five to 10 times the intended mass of the casting to ensure cooling rates high enough for glass formation (38). The wax pattern is then removed either by melting or chemically and the component is centrifugally cast. Finally, the copper mould is etched away to leave the final casting (39). This technique could have widespread application for jewellery. It allows the formation of highly intricate shapes (Figure 1) not achievable with a dividable copper mould, and high form-filling (near 100%), while satisfying the requirements for glass formation. Furthermore, the electroforming and etching procedures mean that the copper is recyclable, and low-cost wax patterns can be easily shaped by an artisanal goldsmith or manufactured at industrial scale (38).

### 1.3 Thermoplastic Forming

Thermoplastic forming (TPF), a method usually reserved for thermoplastic polymers and conventional oxide glasses, can be applied to BMGs. Aside from improved wear resistance, the ability to be so formed is perhaps the most desirable property of BMGs for jewellery. Current

![Fig. 1. Jewellery products cast using the lost-metal mould casting technique similar to conventional investment casting. Reprinted from (37) with permission. Copyright 2013, Santa Fe Symposium](image)
jewellery manufacture is laborious, requiring a highly skilled goldsmith. TPF of hallmark-compliant BMGs offers the potential for fast, economical, large-scale production of jewellery items alongside artisanal design innovations.

To date, BMGs have been successfully shaped via a wide range of TPF techniques such as blow-moulding (50–53), hot-stamping (54–57), extrusion (58–61), hot-rolling (62) and injection-moulding (63). Novel processing possibilities, potentially of use to jewellers for setting gems, include welding and joining methods designed to minimise crystallinity (64–66), as well as the incorporation of second phases when processing in the supercooled liquid region (SCLR) (67).

TPF has many advantages over the direct casting of BMGs and the casting of crystalline metals. It leads to even fewer casting defects than the direct casting of BMGs, since this isothermal process allows the relaxation of internal stresses and elimination of porosity. Porosity can be reduced to levels well below 0.2% (30). TPF can give a wide range of complex, thin-walled and even hollow shapes with high dimensional accuracy (51‒53), as well as surface patterning with nanometre accuracy (55‒57). Recent advances in stretch blow-moulding allow more complex shapes and plastic strains up to several thousand percent (52) compared with a few hundred percent for conventional blow-moulding (50). From a practical perspective, the substantially lower working temperatures and the ability to process platinum- and palladium-based BMGs in air (35) mean that equipment lifetime is extended, costs are lower and manufacture is safer.

Among the many advantages of TPF, the most important is the ability to produce fully glassy samples with dimensions exceeding \( d_c \). This is possible since forming of the final shape and cooling to form the glass are decoupled (34). First, a glassy feedstock material (rods (62), pellets and granules (31, 38), plates (45, 67) or discs (50)) can be cast fully glassy. The feedstock can then be used for TPF to produce a larger component. The use of a pellet feedstock is common practice in polymer processing. It allows fast, easy and economical production since large quantities of simple-shape feedstock can be produced by straightforward casting, while complex shapes are introduced only at the final TPF stage. For Pd-Cu-Si based BMGs, as-cast granules have a SiO\(_2\) surface layer. This is thicker than would otherwise be expected (68) due to the lower surface tension of silicon which promotes segregation to the liquid surface (69). As for gold-based BMGs, this SiO\(_2\) should be removed before TPF to ensure adhesion between the feedstock particles (38, 66).

Since the BMG must be heated above \( T_g \), TPF is possible only within a limited time-temperature processing window before crystallisation occurs (Figure 2). Crystallisation leads to embrittlement,

---

**Fig. 2.** Schematic TTT diagram of a BMG showing the window for thermoplastic processing: (a) initial cooling; (b) further processing. Temperature–time profiles are shown for: A Cooling curve for a fully glassy sample; B critical cooling rate (\( R_c \)) for a fully glassy sample; C thermoplastic processing in the SCLR, with time limited by the onset of crystallisation; D partial crystallisation achieved by annealing in the SCLR.
a loss of thermoplastic formability and of many of the desirable properties associated with the glassy structure (36, 55).

While it would seem logical to perform TPF at temperatures just above $T_g$ to maximise the available processing time, sharp-definition forming requires a low viscosity (below $10^6$ Pa s (45, 70)). As can be seen from a simple treatment of deformation in the SCLR using the Hagen-Poiseuille equation, total deformation increases as the temperature increases (35, 71). As the temperature increases by 20°C, the viscosity, $\eta$, decreases by one order of magnitude, but the time to crystallisation onset, $t_c$, decreases by a factor of three (36). Consequently, the maximum possible deformation increases, as has been confirmed experimentally (71, 72). The best TPF is achieved by heating the feedstock quickly to the highest temperature possible, shaping the low-viscosity supercooled liquid into the desired final product, then quenching back into the glassy state before the onset of crystallisation (35, 73). Given that a more intricate design takes longer to process, there is a desire to increase thermoplastic formability. Strategies being researched include optimisation of fluxing which can widen the SCLR (8, 11, 19), and multi-step thermoplastic processing (74).

By comparison with other BMGs, gold-, platinum- and palladium-based BMGs exhibit exceptional thermoplastic formability (Table I) due to their low $T_g$, high liquid m-fragility, large $\Delta T_x$ and large $S$ (34, 36, 75). Values of $\text{F}_{\text{scan}}$, a parameter that correlates better with deformability during TPF but is more difficult to measure (34, 75), also show that among BMGs, those based on gold, platinum or palladium are the best BMGs for TPF (Figure 3) (75).

TTT curves for crystallisation of BMGs are helpful in comparing their stability during TPF. platinum-based and palladium-based BMGs show excellent stability against crystallisation at high temperatures within the SCLR (Figure 4). As a result, these alloys, alongside zirconium-based BMGs, have been widely used for many TPF experiments reported in the literature (Figure 5), from hot-embossing on the micro- and even nanometre scale (56), to blow-moulding and injection-moulding (52, 77). As examples, BMG watch casings can be made by TPF and machining; those using zirconium-based BMGs are now commercially available, while those using platinum-based BMGs have been made in research laboratories (40).

### 2. Mechanical Properties: Harder Jewellery Alloys Than Ever Before

The jewellery market standard for hardness is a minimum of 100 HV (78). This is still quite soft and so widely used jewellery alloys, with 150–200 HV, scratch relatively easily (Table II). By comparison, BMGs exhibit hardness exceeding 300 HV in the as-cast state. This high hardness offers the opportunity for jewellery with excellent scratch resistance, as well as for watch components (78). The non-crystalline structure of BMGs means that they cannot show the dislocation-mediated
glide and work-hardening familiar for conventional crystalline alloys. When loaded at temperatures below $T_g$, the BMGs are much harder than their crystalline counterparts, but eventually the limit of elasticity is indicated by the local rearrangement of atoms in small 'shear-transformation zones' (STZs) (80, 81). On further loading, the operation of STZs triggers more STZs and there is a plastic instability in which shear is sharply localised in thin bands. These 'shear bands' indicate work-softening.

For most BMGs, a dominant shear band forms under tensile load, leading to macroscopic brittle failure (<1% ductility) (82). Even in the absence of fracture, shear bands lead to readily visible surface marks. In contrast, platinum- and palladium-rich BMGs show remarkably high plasticity in compression and fracture toughness (23, 79, 82–84). As noted in Section 3.1 of Part I (1), these properties are associated with high Poisson ratio of the glass (> 0.41) (85) and with high $m$-fragility of the liquid. In these BMGs, plastic deformation is relatively uniform, occurring through the operation of many shear bands (79). Even for these platinum- and palladium-rich BMGs, however, cold working is not recommended, but jewellery made from them is expected to be particularly durable.

The absence of dislocation-mediated plastic deformation means that BMGs can reach much higher elastic strains than crystalline metals and can approach the theoretical strength (86). The elastic strain limit of BMGs is approximately 2%, six times that of a typical polycrystalline jewellery alloy (approx. 0.3%). BMGs are thus potential hallmark-compliant materials for functional watch components such as springs (23, 30, 40), due to their resulting high resilience ($\sigma_f \varepsilon_f /2$, where $\sigma_f$ and $\varepsilon_f$ are the stress and strain at the elastic limit), representing the capacity for the elastic storage of energy. While their resilience is an order of magnitude higher than other hallmark-compliant materials, it is lower than current spring materials (approx. two-thirds of the resilience of specialist spring materials).

The deformation mechanism in metallic glasses (MGs) relates closely to the glass transition; there is a strong correlation between the hardness of BMGs and their respective glass-transition temperature (12). Both deformation and the glass transition occur via collective atomic motion requiring...
Table II  Typical Hardness Values and Casting Temperatures of Conventional Platinum and Palladium Jewellery Alloysa

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Hallmark</th>
<th>Type</th>
<th>Temperature, °C</th>
<th>Hardness, HV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd-Ru (27)</td>
<td>950Pd</td>
<td>Crystalline</td>
<td>1600</td>
<td>120 (as-cast)</td>
</tr>
<tr>
<td>Pd-Ag-Cu (27)</td>
<td>500Pd</td>
<td>Crystalline</td>
<td>1220</td>
<td>165 (annealed)</td>
</tr>
<tr>
<td>Pt-Ir (27)</td>
<td>950Pt</td>
<td>Crystalline</td>
<td>1790</td>
<td>140 (cold-worked)</td>
</tr>
<tr>
<td></td>
<td>850Pt</td>
<td></td>
<td>1800</td>
<td>110 (annealed)</td>
</tr>
<tr>
<td>Pt-Au (27)</td>
<td>950Pt</td>
<td>Crystalline</td>
<td>1750</td>
<td>300 (age-hardened)</td>
</tr>
<tr>
<td>Pd79Ag3.5P6Si9.5Ge2 (79)</td>
<td>500Pd (90 wt%)</td>
<td>BMG</td>
<td>792</td>
<td>497b (as-cast)</td>
</tr>
<tr>
<td>Pt74.7Cu18.5Ag0.3P18B4Si1.5 (23)</td>
<td>950Pt</td>
<td>BMG</td>
<td>589</td>
<td>395 (as-cast)</td>
</tr>
</tbody>
</table>

aData for platinum- and palladium-based BMGs are shown for comparison.

bDenotes estimate from yield strength.

described as a reduction in ‘free volume’ (100–104), occurs during long sub-$T_g$ annealing, and is associated with hardening (94, 95).

Crystallisation can occur only with a level of atomic mobility equalising or exceeding that necessary for $\alpha$ relaxation. Mostly seen on annealing, crystallisation can also be induced by irradiation, deformation or dealloying. It is classified into polymorphic, eutectic and primary crystallisation (105–107). In the polymorphic and eutectic cases, the crystallised regions have the same composition as the original glass; as crystallisation proceeds, the glass composition stays unaltered. In that case, on annealing at a fixed temperature, the crystal growth rate is constant. In contrast, primary crystallisation involves solute partitioning between crystal and glass; the associated diffusion control tends to limit crystallite size and fine dispersions may be obtained (107). Crystallisation often occurs in many stages, via metastable phase combinations, towards the equilibrium phase mixture.

Partial crystallisation can lead to a dramatic increase in hardness (Figure 6). Despite suggestions that this is due to a phase-mixture effect (108), it can be due to solute enrichment of the glassy matrix, implied by rejection of solute from the growing crystalline phase (90, 109). The increase in hardness is predominantly attributed to the evolution of hard, brittle equilibrium phases, but we also note that crystallisation in Pt49.95Si6.4B24Cu16.65Ge3 led to a rise in $T_g$ and hardness of the remaining glassy matrix due to copper enrichment (from 570 HV to 750 HV) (88).

The equilibrium crystalline phases that form can have complex crystal structures. Although these complex structures may be regarded as beneficial, in that their slow growth should reduce $R_c$ (110–112), they are hard and brittle. Partial crystallisation therefore leads to substantial embrittlement and a fall in fracture toughness
55, 90, 91, 94, 95, 104, 108, 109). Cardinal et al. report that fracture toughness already halves as a result of 20% crystallinity (36, 74). Given the initially high fracture toughness of many platinum- and palladium-rich BMGs (23, 79, 82), substantial increases in hardness could be achieved, without the BMGs becoming too brittle. The potential advantages of partially crystallised systems, which can be regarded as ‘metallic-glass-matrix composites’ (MGMCs), should therefore not be ignored.

Surface crystallisation may lead to enhanced wear resistance. Kazemi et al. report that the surface hardness of their Pt-Cu-Si-B-Ge BMGs can increase to 800 HV while maintaining toughness in the rest of the sample (25). Surface treatments of this kind may be desirable, but the effect of surface crystallisation on other properties must also be considered.

From a scientific perspective, the crystallisation of BMGs is complex due to the simultaneous or stepwise crystallisation of many ordered phases. Their GFA, thermal stability and crystallisation rate are highly dependent on the fluxing procedure (17, 113), due to the effect of lower cooling rates and cleaning of the melt and on sample size due to the statistical probability of a heterogeneous nucleation site (114). On a TTT diagram (Figure 4), crystallisation of a glass during annealing is described by a C-curve (4, 17, 21, 113). The nose of the curve is often sharp since the crystallisation rate may transition over a narrow temperature range from being nucleation-limited to growth-limited (21, 113). Understanding the factors that affect crystallisation and crystallisation steps is particularly important for understanding an alloy’s suitability for TPF where crystallisation can readily occur. During use as jewellery, crystallisation is unlikely as the temperature is well below $T_g$.

3. Tarnishing and Corrosion: No Tarnishing Problem?

Corrosion and tarnishing resistance is key to preserving the lustre of jewellery metals. It is the primary reason why gold and platinum are more highly prized than silver. Resistance to corrosion and tarnishing is also essential to prevent failure due to a deterioration in mechanical properties during use.

Comparing the corrosion resistance of glassy and crystalline alloys is complex and requires consideration of multiple factors. Ideally, a glassy alloy is a defect-free, chemically homogeneous, single-phase material without microstructure. This prevents the formation of local galvanic cells that would accelerate corrosion of less noble phases. Superior corrosion resistance is expected, but glasses are metastable and are therefore in a relatively high-energy state. Thus, they are more chemically active, possibly having corrosion rates higher than their crystalline counterparts (115).

Tarnishing is a well-documented problem for gold-based BMGs; it is the main barrier to their application as a material for jewellery, but to date, there is no industrially viable solution. In general, tarnishing is taken to be a chemical and morphological change of the surface due to
leaching or oxide formation (68). For gold-based BMGs, tarnishing is attributed to the high copper and silicon content of glass-forming compositions (116, 117), and to fast diffusion kinetics aided by the glassy state (118, 119). While the issues of tarnish and corrosion resistance have been well documented for gold-based BMGs, studies of platinum-based and palladium-based BMG alloys remain few.

### 3.1 Corrosion Resistance

Wu et al. compared the corrosion resistance of glassy and crystalline Pd₄₀Ni₄₀P₂₀ (120). The crystalline alloy (formed via vacuum annealing) performed two-to-three times better than the glassy alloy in a range of solutions, due to the presence of several inert phosphides and noble palladium-rich crystalline phases (120). These are the dominant equilibrium phases that form during the crystallisation in many Pt-P and Pd-P-based BMGs (113, 121) so similar corrosion resistance is expected. The formation of an inert surface layer appears critical to corrosion resistance (122). In the corrosion of Pd-Au-Ag-Si BMGs, passivation occurs due to the formation of a palladium-enriched surface layer with underlying silicon-rich glassy phases (123). The resulting anodic passive current density is lower than for SUS 316L stainless steel (123).

Copper-containing BMGs contradict these observations that crystallisation enhances corrosion resistance. Studies of Pd-Cu-Ni-P glasses and their crystalline counterparts in a variety of corrosive solutions show that the heterogeneity of the crystalline material results in an inhomogeneous passive film (124, 125). Subsequent pitting leads to accelerated corrosion (124, 125). During crystallisation, several equilibrium phases, Cu₃Pd, Ni₃Pd₂P, Cu₃Pd₃P₂ and an unknown quaternary phase, form via numerous metastable phases (126). The presence of less noble copper-rich phases amongst noble-metal inert phases leads to galvanic cells and the accelerated corrosion of the copper-rich phases (124). In corrosive chlorinated acidic solutions, copper and nickel dissolution is observed first, followed by the dissolution of palladium and phosphorus. This leaves behind a porous Pd-P network that is gradually dissolved after the outer layers of nickel and copper are removed (125). Dealloying may occur via dissolution of phosphorus followed by the formation of a nanocrystalline Pd-Ni solid solution as ligaments in an initial porous structure (127). Similar pitting was also observed in Pd-Cu-Si alloys (115, 127), suggesting that crystallisation is favourable for corrosion resistance only if the phases that form are all equally inert.

Dealloying in glasses occurs due to preferential leaching out of less noble elements. Their dissolution into the electrolyte allows the remaining noble-metal atoms to rearrange themselves into fine ligaments, resulting in a nanoporous surface (68, 128). Crystallisation due to the deviation from the glass-forming composition, contributes to the formation of ligaments by nucleation and growth of the crystals in the glassy matrix. Compared with dealloying in crystalline alloys, a finer structure is observed in glassy alloys (128). While the resulting nanoporous surface is desirable for catalysis and related applications (128–130), it has a degraded appearance unacceptable for jewellery.

### 3.2 Tarnishing: A Comparison with Gold-Based Bulk Metallic Glasses

Although few studies have compared tarnish resistance, Rizzi et al. reported that a Pd-Cu-Si BMG incubated at 37°C in artificial saliva did not measurably tarnish while a gold-based BMG tarnished significantly (68). Tarnishing of palladium-based BMGs may not be as problematic as for gold-based BMGs (68) but, given the similarities in composition, it is not clear why this is so. Rizzi et al. note the existence of a SiO₂ layer on the surface of both alloys (68). In gold-based BMGs, this SiO₂ layer that forms on casting is an effective diffusion barrier, and prevents tarnishing, but it is quickly worn away and therefore it is not protective (68, 116, 117, 131).

Comparing gold-based BMGs and Pd-Cu-Si-based BMGs, the latter have a $T_g$ that is more than 100 K higher. Atomic diffusion rates, closely linked to $\beta$ relaxation (118, 119, 132–134), when compared at room or body temperature, are therefore likely to be significantly lower in Pd-Cu-Si-based BMGs. This might explain their slower tarnishing. Further studies comparing the behaviour of these alloys are likely to be significant in furthering the understanding of the tarnishing mechanisms of precious-metal-based BMGs.

For Pd/Pt-Ni-P based alloys, there appears to be no tarnishing problem. However, the presence of copper in these alloys impairs corrosion resistance, while replacing it with nickel leads to a lowering of GFA and raises issues of toxicity (36, 123, 135).

Further studies of corrosion and tarnishing of palladium- and platinum-based BMGs at body temperature and in simulated body fluids, such as on gold-based BMGs (38, 68, 116, 117), are required to fully characterise their suitability for
jewellery, as well as for other applications such as in dentistry or as biomaterials (68, 123, 136).

4. Outlook and Future Developments

4.1 Suitability for Jewellery

Aside from the central issue of the conflicting requirements for high fineness and high GFA, BMGs for jewellery offer a wide range of desirable properties. In the as-cast state, they have hardness values that are, at the very least, challenging to achieve in conventional crystalline metals. With values exceeding 300 HV, components made from BMGs are suitable for watchmaking, potentially even as functional components, due to their unique combination of high resilience and hardness. BMGs in jewellery have excellent scratch-resistance, while more intricate, thinner, and even hollow designs are possible because of their high strength.

BMGs offer many processing advantages, both for casting and TPF. The lower casting temperatures of BMGs, alongside the absence of volume shrinkage due to crystallisation, result in relatively few casting-related defects (such as shrinkage and residual stresses), and in possibilities for near-net-shape casting and excellent surface finishes in the as-cast state. While the requirement for fast cooling limits the size, characterised as the critical casting diameter, $d_c$, of fully glassy samples, the attainable dimensions do exceed those required for most jewellery. The difficulties of form-filling, due to viscous melts and to high required cooling rates, have been resolved through new casting techniques. After casting, TPF of samples offers a wealth of new shaping opportunities. TPF may, therefore, enable new jewellery designs as well as economical, highly reproducible mass production.

The corrosion and tarnish resistance of platinum- and palladium-based BMGs are relatively unstudied. From the literature available, tarnishing does not appear to be a significant issue, while corrosion resistance is improved by the presence of noble phases on the surface and is superior to some stainless steels in aggressive environments. While surface coatings may appear to be a solution, inevitable wear leads to accelerated corrosion of any exposed underlying metal.

4.2 Further Work

For platinum- and palladium-based BMGs, the main obstacle to their use in jewellery is the need to achieve fully glassy states with over 95 wt% platinum or palladium. Achieving such high fineness while alloying sufficiently to achieve adequate GFA appears, at best, challenging. The development of platinum- and palladium-based BMGs with precious-metal content exceeding 90 wt% and even 95 wt% (23, 79) does, however, give hope. Compositions that would give 950Pt and 950Pd BMGs are expected to show high liquid fragilities and therefore low GFA is expected.

In the search for higher precious metal contents, microalloying appears a key strategy, although its effects are far from fully understood. A deeper understanding of microalloying effects may assist in optimising GFA, but the restrictions imposed by hallmark-compliance mean that extensive microalloying can only be with lighter elements (to maximise the weight percent of platinum or palladium) and so other avenues should also be considered. MGMCs may offer opportunities to raise the precious metal content without sacrificing GFA or leading to a heterogeneous appearance (137).

Fluxing of the melt, to remove oxide particles that may act as heterogeneous nucleation sites, has a dramatic effect on GFA: optimised processing can increase critical casting thicknesses from the millimetre to the centimetre scale (8, 11, 18, 19). But treatment of some palladium- and platinum-based BMG-forming liquids with the usual $B_2O_3$ flux can lead to undesirable contamination with boron (23, 40, 79, 138). There is a clear need for the development of more stable fluxes and opportunity for optimisation of fluxing treatments.

Compared to 950Pt BMGs, 950Pd BMGs are even more challenging to achieve. From the compositions reported (Table III), further exploration of Pd-Cu-Si alloys should be considered. While Demetriou et al.’s palladium-based BMG exhibits exceptional mechanical properties, compositions such as Pd$_{79}$Cu$_{10}$Si$_{10}$P$_5$ (138) show higher GFA and higher weight fractions of palladium, due to a smaller degree of required alloying with metalloids. They, therefore, appear a promising area for further study in pursuit of hallmark-compliant BMGs. The Pd-Si binary system (specifically Pd$_{61}$Si$_{19}$) is one of the best binary glass-forming systems known (142, 143), due to a large energy barrier to crystallisation (142). As for Pd-P-based BMGs, these compositions have liquids of high $m$-fragility. With palladium content raised to 95 wt%, the $m$-fragility is likely to be even higher, resulting in reduced GFA. But, there are still many possibilities for a potential 950Pd hallmark-compliant BMG.

Lastly, for platinum- and palladium-based BMGs to be applicable in jewellery, they must maintain
<table>
<thead>
<tr>
<th>Alloy, at%</th>
<th>Precious metal content, wt%</th>
<th>Contains nickel</th>
<th>T_gr K</th>
<th>T_xf K</th>
<th>ΔT_x K</th>
<th>T_σf K</th>
<th>d_gr mm</th>
<th>T_rg</th>
<th>S</th>
<th>Hardness, HV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt66Cu20P20 (30, 121)</td>
<td>86.1</td>
<td>No</td>
<td>522</td>
<td>580</td>
<td>58</td>
<td>850</td>
<td>12</td>
<td>0.61</td>
<td>0.18</td>
<td>–</td>
</tr>
<tr>
<td>Pt60Cu22Pt2 (30, 36)</td>
<td>86.6</td>
<td>No</td>
<td>506</td>
<td>568</td>
<td>63</td>
<td>881</td>
<td>16</td>
<td>0.58</td>
<td>0.17</td>
<td>402</td>
</tr>
<tr>
<td>Pt57.5Cu14.5Ni5.3P22.5 (30, 121)</td>
<td>86.3</td>
<td>Yes</td>
<td>508</td>
<td>606</td>
<td>98</td>
<td>795</td>
<td>16</td>
<td>0.64</td>
<td>0.34</td>
<td>402</td>
</tr>
<tr>
<td>Pt52.5Cu22Ni5.5P21 (30, 121)</td>
<td>75.9</td>
<td>Yes</td>
<td>515</td>
<td>589</td>
<td>74</td>
<td>873</td>
<td>20</td>
<td>0.59</td>
<td>0.21</td>
<td>392</td>
</tr>
<tr>
<td>Pt50Cu2NiP22 (121)</td>
<td>87.0</td>
<td>No</td>
<td>506</td>
<td>569</td>
<td>63</td>
<td>881</td>
<td>16</td>
<td>0.58</td>
<td>0.17</td>
<td>–</td>
</tr>
<tr>
<td>Pt74.7Cu1.5Ag0.3P18B4Si1.5 (23)</td>
<td>95.0</td>
<td>No</td>
<td>479</td>
<td>529</td>
<td>50</td>
<td>862</td>
<td>2</td>
<td>0.56</td>
<td>0.13</td>
<td>395</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Alloy, at%</th>
<th>Precious metal content, wt%</th>
<th>Contains nickel</th>
<th>T_gr K</th>
<th>T_xf K</th>
<th>ΔT_x K</th>
<th>T_σf K</th>
<th>d_gr mm</th>
<th>T_rg</th>
<th>S</th>
<th>Hardness, HV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt62.5Si10.5B19.5Cu17.5 (30)</td>
<td>86.4</td>
<td>No</td>
<td>581</td>
<td>603</td>
<td>22</td>
<td>951</td>
<td>2–5</td>
<td>0.61</td>
<td>0.06</td>
<td>–</td>
</tr>
<tr>
<td>Pt69.9Si6.5B24Cu2.65Ge3 (30)</td>
<td>85.0</td>
<td>No</td>
<td>579</td>
<td>634</td>
<td>55</td>
<td>928</td>
<td>5</td>
<td>0.61</td>
<td>0.16</td>
<td>570</td>
</tr>
</tbody>
</table>

### Palladium-phosphorus-based BMGs

<table>
<thead>
<tr>
<th>Alloy, at%</th>
<th>Precious metal content, wt%</th>
<th>Contains nickel</th>
<th>T_gr K</th>
<th>T_xf K</th>
<th>ΔT_x K</th>
<th>T_σf K</th>
<th>d_gr mm</th>
<th>T_rg</th>
<th>S</th>
<th>Hardness, HV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd30Ni30P20 (2, 121)</td>
<td>71.0</td>
<td>Yes</td>
<td>590</td>
<td>671</td>
<td>91</td>
<td>970</td>
<td>10</td>
<td>0.61</td>
<td>0.24</td>
<td>538</td>
</tr>
<tr>
<td>Pd30Ni29Cu30P20 (19, 121)</td>
<td>60.3</td>
<td>Yes</td>
<td>572</td>
<td>670</td>
<td>98</td>
<td>836</td>
<td>72</td>
<td>0.56</td>
<td>0.37</td>
<td>515</td>
</tr>
<tr>
<td>Pd33Ni10Cu27P20 (17, 21)</td>
<td>63.6</td>
<td>Yes</td>
<td>585</td>
<td>716</td>
<td>131</td>
<td>878</td>
<td>30</td>
<td>0.67</td>
<td>0.45</td>
<td>–</td>
</tr>
<tr>
<td>Pd42.5Cu30Ni7.5P20 (18)</td>
<td>62.3</td>
<td>Yes</td>
<td>575</td>
<td>684</td>
<td>109</td>
<td>800</td>
<td>80</td>
<td>0.72</td>
<td>0.48</td>
<td>–</td>
</tr>
<tr>
<td>Pd30Pt17.5Cu32.5P20 (136)</td>
<td>34.4</td>
<td>No</td>
<td>541</td>
<td>622</td>
<td>81</td>
<td>812</td>
<td>50</td>
<td>0.67</td>
<td>0.30</td>
<td>–</td>
</tr>
<tr>
<td>Pd35Pt15Cu30P20 (36, 139, 140)</td>
<td>40.6</td>
<td>No</td>
<td>551</td>
<td>624</td>
<td>73</td>
<td>847</td>
<td>30</td>
<td>0.65</td>
<td>0.25</td>
<td>460</td>
</tr>
<tr>
<td>Pd20Pt20Cu20Ni20P20 (121)</td>
<td>25.1</td>
<td>Yes</td>
<td>580</td>
<td>645</td>
<td>65</td>
<td>820</td>
<td>10</td>
<td>0.71</td>
<td>0.27</td>
<td>–</td>
</tr>
<tr>
<td>Pd79Ag3P6Si6.5Ge2 (79)</td>
<td>89.6</td>
<td>No</td>
<td>613</td>
<td>644</td>
<td>31</td>
<td>1065</td>
<td>6</td>
<td>0.58</td>
<td>0.07</td>
<td>497b</td>
</tr>
<tr>
<td>Pd30Ni30SiP2 (7)</td>
<td>71.1</td>
<td>Yes</td>
<td>579</td>
<td>688</td>
<td>104</td>
<td>971</td>
<td>&gt;10</td>
<td>0.60</td>
<td>0.27</td>
<td>556b</td>
</tr>
</tbody>
</table>

### Palladium-silicon-based BMGs

<table>
<thead>
<tr>
<th>Alloy, at%</th>
<th>Precious metal content, wt%</th>
<th>Contains nickel</th>
<th>T_gr K</th>
<th>T_xf K</th>
<th>ΔT_x K</th>
<th>T_σf K</th>
<th>d_gr mm</th>
<th>T_rg</th>
<th>S</th>
<th>Hardness, HV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd78Si1.7Cu5 (42)</td>
<td>91.3</td>
<td>No</td>
<td>635</td>
<td>683</td>
<td>49</td>
<td>1098</td>
<td>3</td>
<td>0.58</td>
<td>0.11</td>
<td>527b</td>
</tr>
<tr>
<td>Pd78Si1.7Ag5 (42)</td>
<td>89.1</td>
<td>No</td>
<td>636</td>
<td>690</td>
<td>54</td>
<td>1107</td>
<td>4</td>
<td>0.58</td>
<td>0.11</td>
<td>537b</td>
</tr>
<tr>
<td>Pd23Si1.7AgCu5 (36)</td>
<td>85.3</td>
<td>No</td>
<td>637</td>
<td>703</td>
<td>66</td>
<td>1175</td>
<td>3</td>
<td>0.54</td>
<td>0.12</td>
<td>542b</td>
</tr>
<tr>
<td>Pd75Si1.7AgCu5 (36)</td>
<td>86.9</td>
<td>No</td>
<td>625</td>
<td>692</td>
<td>67</td>
<td>1063</td>
<td>5</td>
<td>0.59</td>
<td>0.15</td>
<td>532b</td>
</tr>
<tr>
<td>Pd75Si1.7AgCu5 (42)</td>
<td>87.7</td>
<td>No</td>
<td>633</td>
<td>704</td>
<td>71</td>
<td>1148</td>
<td>4</td>
<td>0.55</td>
<td>0.14</td>
<td>538b</td>
</tr>
<tr>
<td>Pd75Si1.7AgCu5 (42)</td>
<td>88.5</td>
<td>No</td>
<td>619</td>
<td>696</td>
<td>77</td>
<td>1050</td>
<td>5</td>
<td>0.59</td>
<td>0.18</td>
<td>517b</td>
</tr>
<tr>
<td>Pd75Si1.7AgCu5 (42)</td>
<td>86.2</td>
<td>No</td>
<td>620</td>
<td>691</td>
<td>71</td>
<td>1034</td>
<td>7</td>
<td>0.60</td>
<td>0.17</td>
<td>513b</td>
</tr>
<tr>
<td>Pd75Si1.7AgCu5 (42)</td>
<td>87.0</td>
<td>No</td>
<td>621</td>
<td>695</td>
<td>74</td>
<td>1029</td>
<td>10</td>
<td>0.60</td>
<td>0.18</td>
<td>536b</td>
</tr>
<tr>
<td>Pd79Cu5Si10P5 (138, 141)</td>
<td>91.1</td>
<td>No</td>
<td>609</td>
<td>682</td>
<td>73</td>
<td>995</td>
<td>5</td>
<td>0.61</td>
<td>0.19</td>
<td>492b</td>
</tr>
<tr>
<td>Pd79Cu5Ag5Si10P5 (141)</td>
<td>90.7</td>
<td>No</td>
<td>614</td>
<td>684</td>
<td>70</td>
<td>1001</td>
<td>4</td>
<td>0.61</td>
<td>0.18</td>
<td>–</td>
</tr>
<tr>
<td>Pd79Cu5Ag5Si10P5 (141)</td>
<td>90.3</td>
<td>No</td>
<td>613</td>
<td>684</td>
<td>71</td>
<td>1005</td>
<td>5</td>
<td>0.61</td>
<td>0.18</td>
<td>–</td>
</tr>
<tr>
<td>Pd79Cu5Ag5Si10P5 (141)</td>
<td>90.8</td>
<td>No</td>
<td>610</td>
<td>683</td>
<td>73</td>
<td>1005</td>
<td>5</td>
<td>0.61</td>
<td>0.18</td>
<td>–</td>
</tr>
<tr>
<td>Pd79Cu5Ag5Si10P5 (141)</td>
<td>94.9</td>
<td>No</td>
<td>611</td>
<td>676</td>
<td>65</td>
<td>1006</td>
<td>7</td>
<td>0.61</td>
<td>0.16</td>
<td>–</td>
</tr>
<tr>
<td>Pd79Cu5Au2Ag2Si10P5 (141)</td>
<td>87.8</td>
<td>No</td>
<td>617</td>
<td>670</td>
<td>53</td>
<td>1020</td>
<td>3</td>
<td>0.60</td>
<td>0.13</td>
<td>–</td>
</tr>
<tr>
<td>Pd79Cu5Au2Ag2Si10P5 (141)</td>
<td>88.2</td>
<td>No</td>
<td>613</td>
<td>676</td>
<td>63</td>
<td>1021</td>
<td>4</td>
<td>0.60</td>
<td>0.15</td>
<td>–</td>
</tr>
<tr>
<td>Pd79Cu5Au2Ag2Si10P5 (141)</td>
<td>88.6</td>
<td>No</td>
<td>617</td>
<td>683</td>
<td>66</td>
<td>1014</td>
<td>3</td>
<td>0.61</td>
<td>0.17</td>
<td>–</td>
</tr>
<tr>
<td>Pd79Cu5Au2Ag2Si10P5 (141)</td>
<td>89.0</td>
<td>No</td>
<td>618</td>
<td>689</td>
<td>71</td>
<td>1015</td>
<td>5</td>
<td>0.61</td>
<td>0.18</td>
<td>–</td>
</tr>
<tr>
<td>Pd79Au5Ag5Si16.5 (140)</td>
<td>88.6</td>
<td>No</td>
<td>636</td>
<td>685</td>
<td>49</td>
<td>–</td>
<td>3</td>
<td>–</td>
<td>–</td>
<td>500b</td>
</tr>
</tbody>
</table>

*a ΔT_x, T_σf, d_gr, and S parameters are given to compare their thermal stability, GFA and thermoplastic formability. Values of d_gr should be treated with caution, since they are dependent on the processing method as well as on T_gr.

b Denotes an estimate of hardness from compressive yield stress or yield strength.
their lustre. Limited work has been carried out to assess how they may tarnish or corrode over time. Further studies of their performance in simulated body fluids at body temperature are necessary to evaluate their suitability. Such studies may also assist in the development of tarnish-resistant 18 karat gold-based BMGs.

5. Conclusions

Hallmark-compliant BMGs exhibit improved hardness and elasticity over conventional crystalline alloys, leading to much-improved wear resistance for jewellery, watch casings and even functional components in watches. Their lower casting temperatures, minimal shrinkage on casting and thermoplastic formability facilitate high-definition near-net-shape casting with few casting defects and processability via methods usually reserved for polymers and conventional oxide glasses. Consequently, BMGs based on precious metals should be of significant interest in jewellery.

The platinum- and palladium-based BMGs reviewed here show some of the best mechanical properties and highest GFA amongst all known BMGs. Their high plasticity is associated with the high m-fragility of their liquids and thereby also with exceptional thermoplastic formability, superior to any other family of BMGs. Compared with 18 karat gold-based BMGs, the absence of any tarnishing problem is advantageous. However, the strict hallmarking standards for platinum and palladium alloys in jewellery mean that the extent of alloying is restricted. Increasing platinum- and palladium- content to the required high levels appears to lead to a reduction in GFA. This reduction may, in part, be due to such melts having higher m-fragility, but changes in crystallisation behaviour may also play a significant role. Specifically, it is challenging to achieve sufficient GFA to obtain BMGs with the compositions that would be most desirable for jewellery (950Pd or 950Pt). A deeper understanding and subsequent optimisation of microalloying and fluxing procedures are suggested as further areas of study for improvements to GFA in these platinum- and palladium-rich systems.

Acknowledgements

OSH thanks the Goldsmiths’ Company Assay Office, London UK, for financial support and Dr Christopher Corti for useful discussions. ALG acknowledges support from the European Research Council under grant ERC-2015-AdG-695487 (ExtendGlass).

References

The Authors

Owain Houghton is a PhD student at the University of Cambridge, UK. He obtained a BA degree in Natural Sciences and an MSci degree in Materials Science from the same institution. He researches bulk metallic glasses based on precious metals and their potential applications for jewellery as a member of the Microstructural Kinetics Group.
A. Lindsay Greer is a professor of Materials Science at the University of Cambridge. He received MA and PhD degrees from Cambridge and holds Honorary Doctorates from AGH University of Science and Technology, Cracow, Poland, and the University of Sofia, Bulgaria. He was an assistant professor at Harvard University, USA; has held visiting positions in Grenoble, France; St. Louis, USA; Vienna, Austria; and Turin, Italy; and is a foreign principal investigator in the Advanced Institute for Materials Research, Tohoku University, Japan. He leads the Microstructural Kinetics Group, and his current research focuses mainly on metallic glasses. He is a coauthor of some 450 papers.
Platinum-based alloys are being developed for high-temperature applications with the aim of replacing some of the currently used nickel-based superalloys (NBSAs) and benchmark alloy, PM2000. The platinum-based superalloys have a similar structure to the NBSAs and can potentially be used at higher temperatures and in more aggressive environments because platinum is more chemically inert and has a higher melting point. In this paper, the recent progress in research and development of platinum-based superalloys is overviewed. Firstly, the composition optimisation and structural design of platinum-base superalloys are introduced. The structural characteristics, mechanical properties, oxidation resistance and corrosion behaviour of platinum-aluminium ternary, quaternary and multiple superalloys are summarised. Finally, directions for further research and application of platinum-based superalloys are analysed and prospected.

**1. Introduction**

Components in many different applications at high temperature and in corrosive environments require materials with excellent high temperature mechanical properties and chemical resistance. Aerospace applications represent an extremely challenging field, for the development of new materials, and for the improvement of the existing ones (1). NBSAs with the Ni3Al intermetallic compounds as the main strengthening phase have been widely used in high-temperature components such as aeroplane engines, industrial gas turbine blades and modern industry fields. After decades of development, the working temperature of NBSAs is about 1100°C (2) and can reach up to 1150°C (3, 4). Recently, a new platinum-modified nickel-base alloy with exceptional high temperature stability has been identified (5, 6). Coarsening studies conducted reveal unusually high volume fractions of morphologically stable γ’ precipitates up to 1200°C, which suggests that the alloy would have excellent performance as a bond coat or single crystal blade. A further increase in the operating temperature of the gas turbine will improve the combustion efficiency, reduce fuel consumption and CO2 emissions, and leads to higher thrust values (7, 8). NBSAs operating temperature is approximately 85% of their melting point. An increasing interest has been shown in developing new alloys based on materials with higher melting points with similar structure to that of NBSAs and capable of being used at 1300°C (9, 10).

Potential candidate materials that may replace NBSAs or iron-based superalloys such as PM2000 mainly include intermetallic compounds, ceramics and ceramic matrix composites, refractory metals and high melting point platinum group metals (11). Some high melting point intermetallic compounds have high-temperature strength, lower diffusion
rate and excellent corrosion resistance. However they lack plasticity or fracture toughness at room temperature (12, 13). Components based on ceramics and ceramic matrix composites have high-temperature strength, creep resistance, oxidation resistance and corrosion resistance which are attractive for their potential use in gas turbine engines. Unfortunately, low fracture toughness and brittle behaviour usually associated with ceramics are problems for high-temperature applications. Refractory metals and their alloys have high melting temperatures and for this reason researchers are considering the possibility of using them in the hot parts of gas turbines to replace NBSAs. These refractory metals and alloys lack sufficient oxidation resistance which limits their practical application (14). Superalloys based on platinum group metals (platinum, iridium, rhodium) show extremely strong chemical stability and two-phase structure (face-centred cubic (fcc)/L12), which makes this group of alloys a potential candidate to be developed as high-temperature materials for next-generation gas turbines (15–22). However, the main weaknesses of most iridium-based and rhodium-based refractory superalloys are brittleness, high cost and high density.

Unlike iridium and rhodium, platinum has become an essential high-temperature material in special applications. It has a higher melting point than nickel (platinum = 1769°C, nickel = 1453°C), better oxidation resistance, corrosion resistance, chemical stability and does not require coating protection when used at high temperatures (23, 24). Platinum-based alloys have excellent mechanical properties such as high creep strength and ductility, which make them have application potential in the fields of chemical engineering, space technology and glass industry (24, 25). At this time, the research on platinum-based superalloys includes solid solution strengthened, dispersion strengthened and precipitation strengthened alloys as well as platinum group metal compounds (26). Current usage is restricted to solid solution strengthened alloys and dispersion strengthened alloys, the latter being classified as part of the group of composite materials. Solid solution strengthened platinum-based alloys are a family of alloys which have been researched and developed for some time. The compositions and preparation process can be said to be more mature.

All transition group elements have considerable solid solubility in platinum. The elements near platinum in the periodic table form a continuous solid solution with platinum and have different degrees of solid solution strengthening effect on the platinum matrix. At high temperatures, ruthenium, iridium and rhodium have higher tensile strength than platinum and palladium. The high temperature durability and creep rupture strength of iridium are also much higher than that of Pt-Rh alloys. Ruthenium, iridium, rhodium and palladium have become the main solid solution strengthening elements. According to the relationship between stacking fault energy and creep rate, ruthenium and iridium have the largest solid solution strengthening effect on platinum, followed by rhodium, and palladium with the smallest effect (27).

Currently, the research and development on platinum-based solid solution alloys mainly include binary alloys such as Pt-Rh, Pt-Ir, Pt-Ru, Pt-Ni, Pt-W and ternary alloys such as Pt-Pd-Rh and Pt-Rh-Ru (28). The properties of Pt-Rh alloys are the most stable: an increase in rhodium content leads to higher temperature durability, extended creep life and decreased creep rate (29). However, the improvement of mechanical properties decreases when rhodium content exceeds 30 wt%. In addition, machinability is significantly worse at these levels of rhodium content. The high temperature durability, creep life and creep rate of Pt-Ir alloy are better than the Pt-Rh alloy. On the other hand, Pt-Ir alloys tend to have higher weight losses in oxidising environments above 1100°C due to the selective oxidation of iridium after prolonged exposure to such atmospheres. In addition, for solid-solution strengthened Pt-Rh alloys, the coarsening of crystal grains at high temperatures will lead to reduced alloy strength and premature failure of components.

In order to improve the high-temperature mechanical properties of platinum-based alloys, oxide dispersion strengthened (ODS) alloys with ZrO2 or Y2O3 as reinforcing phase have been researched and developed (30, 31). The fine oxide particles dispersed in the platinum matrix can stabilise the grain boundaries, prevent the movement of dislocations and improve the high temperature fracture strength. However, these ODS alloys have great brittleness, crack sensitivity and cannot withstand severe temperature changes. A particular type of ODS alloys has been developed, namely dispersion hardened platinum (DPH) alloys (32). These alloys are reinforced by dispersion of oxides formed inside the alloy via an internal oxidation process of pure oxygen-reactive elements (i.e., elements with high affinity to oxygen such as cerium, yttrium, scandium and zirconium). These elements are added to the melt and their oxidation is
subsequently obtained by appropriate treatments. The stress-fracture strength of DPH alloys is further improved with respect to solution strengthened alloys. For instance, the stress-fracture strength of DPH platinum is higher than that of Pt-10Rh alloy (33), with good plasticity. However, the production process of all the dispersion strengthened alloy families is complicated and problems may arise during welding operations. The strength of the welded joint tends to drop due to excessive formation of oxide particles during welding (24).

Precipitation strengthening is the main strengthening mechanism of platinum-based superalloys currently under research and development. These alloys show higher temperature strength than solution strengthened and dispersion strengthened alloys at 1300°C (34–39). However, high density and cost are the major drawbacks to the use of platinum, but it is likely that the platinum-based alloys can be used for the highest application temperature components (10, 40). Due to the excellent properties of oxidation and corrosion resistance, the Pt-Al system superalloys could have potential as coatings on NBSAs or other substrates (10, 22, 41). Their density can be slightly reduced by adding suitable light alloying elements, while the high performance and recyclability of platinum-based alloys make up for the high price (42). This paper summarises the research status and progress of platinum-based superalloy materials. Firstly, we introduce the composition and structural optimisation design of platinum-based superalloys, the structural characteristics and evolution of Pt-Al-based ternary, quaternary and multi-element superalloys, and their mechanical properties, oxidation and corrosion resistance behaviours. The strengthening mechanisms, the relationship between oxidation, corrosion and alloy composition have been analysed and the results will be presented and discussed. Finally, further research and application prospects of platinum-based superalloys are analysed and discussed.

2. Structure and Composition Design of Platinum-Based Superalloys

A large number of new alloys have been researched and developed based on strong demand for higher working temperature and high temperature resistant structural materials in the aerospace field. The goal of the research is to seek a material with better high-temperature mechanical properties (tensile, fracture, creep and thermomechanical fatigue properties) and environmental stability (resistance to high-temperature oxidation and hot corrosion) than nickel-based superalloys (43). Inspired by the successful experience of precipitation strengthening obtained in the γ matrix (fcc structure) of nickel-based superalloys, much effort is now put into the research and development of platinum-based superalloys with similar structures to the γ/γ' system found in nickel-based superalloys (7). Research on platinum-based superalloys began at the end of the 20th century. The initial work was mainly on structure and composition design, including the formation of a Pt3X (γ') precipitation strengthening phase and the selection of solid solution strengthening elements.

2.1 Second Phases and Possible Reinforcement

Platinum can form Pt3X and Pt5X high melting point intermetallic compounds on the platinum-rich side of the phase diagram with transition metals and rare earth metals (44), such as Pt3Al (1550°C), Pt3Hf (2250°C), Pt3Sc (1850°C), Pt3Y (2020°C) and Pt3Zr (2250°C). Their melting points are higher than Ni3Al (1390°C). Most platinum compound precipitation phases with γ' structure have a high melting point, high thermal conductivity, low thermal expansion coefficient, high strength and a large number of possible slip systems. It can be expected that γ/γ' platinum alloys will have high thermal strength and precipitation strengthening effects, leading to the possible development of a new generation of precipitation strengthened platinum-based superalloys (45). Figure 1 represents the binary Pt-Al phase diagram (44). The diagram shows that the maximum solubility of aluminium in platinum is about 10 at% at relatively low temperatures, whereas at the eutectic temperature (1507°C) the value is slightly higher. The Pt3Al phase forms at the eutectic temperature and the eutectic reaction can be found in the top right of the diagram. At high temperatures, the Pt3Al intermetallic compound shows a L1_2 structure. It transforms into a tetragonal structure (D0_1c) at lower temperatures. Pt3Al is the most important intermetallic phase. Table I lists the common precipitation phases and main performance evaluations in platinum-based alloys (46). The Pt3X phase mainly appears in platinum-transition metals and platinum-simple metal alloy systems, while Pt3X mainly appears in platinum-rare earth and platinum-alkaline earth metal alloy systems. The Pt3X phase formed by chromium, vanadium and platinum decomposes at 1130°C and 1015°C respectively, and was excluded from the design study of platinum-based
Table I Candidate Elements to Form Pt$_3$X Precipitates (46)

<table>
<thead>
<tr>
<th>Element</th>
<th>Structure of Pt$_3$X</th>
<th>Melting range, °C</th>
<th>Environmental resistance</th>
<th>Density, g cm$^{-3}$</th>
<th>Attributes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium</td>
<td>Low temperature: tetragonal (D024) High temperature: fcc (L1$_2$)</td>
<td>1500–1769</td>
<td>Good oxidation resistance. Forms stable external Al$_2$O$_3$ scale which protects the metal from internal oxidation</td>
<td>2.7</td>
<td>Low density. Transformation of Pt$_3$Al at 1290°C. Good oxidation resistance. Lowers solidus temperature</td>
</tr>
<tr>
<td>Titanium</td>
<td>Tetragonal (D024) at stoichiometric compositions; fcc (L1$_2$) in platinum-rich alloys</td>
<td>1769–1800</td>
<td>Prone to oxidation even at low temperatures</td>
<td>4.5</td>
<td>L1$_2$ structure. Favourable density. Increases solidus temperature</td>
</tr>
<tr>
<td>Vanadium</td>
<td>Fcc (L1$_2$)</td>
<td>1769–1805</td>
<td>Vanadium absorbs relatively large amounts of oxygen</td>
<td>5.8</td>
<td>The Pt$_3$V phase is only stable to 1015°C</td>
</tr>
<tr>
<td>Chromium</td>
<td>Fcc (L1$_2$)</td>
<td>1769–1785</td>
<td>Chromium has a beneficial effect on hot corrosion and oxidation resistance</td>
<td>7.19</td>
<td>The Pt$_3$Cr phase is only stable to 1130°C</td>
</tr>
<tr>
<td>Gallium</td>
<td>Fcc (L1$_2$)</td>
<td>1373–1769</td>
<td>The effect of gallium additions on high temperature oxidation of alloys is uncertain</td>
<td>5.91</td>
<td>Low melting temperature</td>
</tr>
<tr>
<td>Yttrium</td>
<td>Fcc (L1$_2$). No two-phase (Pt)$+$Pt$_3$Y region because of the Pt$_3$Y phase</td>
<td>1615–1769</td>
<td>The effect of major yttrium additions on the environmental behaviour of alloys has not been documented</td>
<td>4.5</td>
<td>Highly reactive and difficult to process</td>
</tr>
<tr>
<td>Zirconium</td>
<td>Tetragonal (D024) at stoichiometric compositions. Fcc (L1$_2$) in platinum-rich alloys</td>
<td>1769–1963</td>
<td>Exposure to oxygen causes embrittlement due to the formation of brittle oxides</td>
<td>6.4</td>
<td>L1$_2$ structure. Generally embrittling in alloys. Susceptible to oxidation</td>
</tr>
</tbody>
</table>

(Continued)
superalloys. Although tin, lead, gallium and other elements can form a L1_2 structure phase with platinum, they are also excluded due to the low melting point. Initial research on binary systems such as Pt-Zr, Pt-Hf and ternary system alloys such as Pt-Rh-Zr, Pt-Rh-Hf showed that γ’ phases Pt_3Zr and Pt_3Hf are formed in the alloy which are coherent with the matrix (47). The presence of zirconium and hafnium as solid solution strengthening elements in combination with γ’ precipitation strengthening give these alloys high-temperature mechanical properties, but they all have the problem of poor oxidation resistance. The formation of brittle zirconium and hafnium oxides leads to embrittlement of the material (48).

The refractory metals tantalum and niobium can increase the solidus temperature of platinum-based superalloys and are worthy of further study. Alloying with aluminium leads to the formation of Pt_3Al, a strengthening intermetallic of the Pt_3X type that has two different crystal structures: the cubic structure (L1_2) at high temperatures and allotrope tetragonal structure (D0_24) at low temperatures. The high-temperature allotrope can be stabilised at lower temperatures by adjusting the composition of the alloy matrix.

It is necessary to study the structure and properties of the Pt_3X second phase particles in order to develop precipitation strengthened platinum-based superalloys. However, there are few reports on the experimental measurement of the mechanical properties of Pt_3X intermetallic compounds. Adjal (49), Pan (50) and Li (51) investigated the electronic structure, thermodynamic properties, oxidation resistance and mechanical properties of Pt_3X intermetallic compounds by simulation calculation methods. The mechanical properties and anisotropy of Pt_3M alloy were determined from these studies. The anisotropy is mainly derived from the d electronic state of platinum and the d electronic state (or p electronic state) of M. Pt_3Hf has the highest modulus (bulk modulus, shear modulus, Young’s modulus) and hardness, while Pt_3Y has the lowest values (51). Liu (52) used first-principles calculations to study the effect of pressure on the structure and mechanical properties of Pt_3Al. The study found the elastic modulus, bulk modulus and shear modulus of Pt_3Al increase linearly with increasing pressure. Pt_3Al changes from tetragonal to cubic structure when the pressure reaches 60 MPa, indicating that the cubic structure of Pt_3Al has higher resistance to volume deformation.

### 2.2 Alloy Composition Design

Table II lists the candidate solid solution strengthening elements and main performance evaluations of platinum-based superalloys (46). Platinum group metals ruthenium, iridium, rhodium, palladium, nickel and rhenium can all be used as solid solution strengthening elements.
The alloys Pt-Al-Ni, Pt-Al-Ru, Pt-Al-Cr, Pt-Al-Ti, Pt-Al-Re, Pt-Ti-Ru, Pt-Ti-Re, Pt-Ta-Ru, Pt-Ta-Re and Pt-Nb-Ru were selected through the comprehensive evaluation of precipitation strengthening, solid solution strengthening and alloy properties. These alloys were optimised and screened and are all characterised by a fcc (platinum) solid solution matrix and fcc \((L_1^2)\) \(Pt_3X\) precipitation phase, thus a two-phase microstructure. Investigations on structural composition, mechanical properties and oxidation resistance were performed. The results showed that the two-phase structure of Pt-Al-X and Pt-Ti-X alloys confers significant precipitation strengthening, with hardness exceeding 400 Vickers hardness (HV1) and strong resistance to crack initiation and propagation. Aluminium-containing alloys also have better oxidation resistance than the other alloys due to the formation of an aluminium oxide-based protective film on the surface. Internal oxidation was observed in titanium-containing alloys. Therefore, aluminium is considered to be a necessary alloying element for the development of oxidation-resistant platinum-based superalloys (46, 53). For these reasons, the subsequent research mainly focuses on the Pt-Al-X alloy system.

### 3. Pt-Al-X Ternary Alloy

#### 3.1 Structural Characteristics of Ternary Alloys

In order to obtain an effective strengthening effect on platinum-based ternary alloys it is necessary to determine the low-temperature structure of the \(Pt_3Al\) phase in the representative binary alloy. Wolff (22) used an electric arc furnace (EAF) to smelt the Pt-12Al (at%) alloy and the material was then subjected to 96 h solution annealing and subsequent ageing at 1350°C. **Figure 2** shows some structural features of the Pt-12Al alloy. It can be seen that Pt-Al precipitation phase exhibits strong directional cubic alignment and the dispersed sub-micron nature of the precipitation phase exhibits a typical bimodal size distribution. This special-orientation geometrical configuration is a highly coherent phase which has low mismatch strain. The Pt-Al-\(\gamma'\) phase additionally has a low-temperature variant and a lath or twin structure. The maximum volume fraction of the Pt-Al phase is limited to about 30% due to the maximum solubility of aluminium in platinum. The volume ratio of the precipitation phase in nickel-based superalloys is significantly lower than in Pt-Al alloys.
superalloys can be as high as 70–80%. Additional information about the microstructural features of Pt₃Al can be inferred from Figure 3 where a transmission electron microscopy (TEM) bright-field image microstructure characteristic of the precipitate phase in an alloy with slightly higher aluminium content, namely Pt-14Al (at%) alloy (54). It can be seen from Figure 3 that the martensitic transformation has occurred in the platinum matrix leading to the formation of a clear stacked sheet or plate-like structure. Electron diffraction analysis shows that the stacked plates are twinned with each other, the [001] directions of adjacent tetragonal structure D₀’c single packages are perpendicular to each other, and the twin planes are (112) planes. The [001] direction of D₀’c is parallel to the <001> direction of the cubic matrix.

Adding transition metals such as nickel, titanium, chromium, ruthenium, iridium, rhenium and tantalum to Pt-Al alloys can improve the strengthening effect of γ’(Pt₃Al) precipitates, thermal stability, solid solution strengthening of the matrix and overall properties. Several typical ternary alloy microstructures are shown in Figure 4. The two-phase structure of Pt₃Al and platinum solid solution of all alloys has been confirmed by X-ray diffraction (XRD) experiments (55). The alloys with nominal compositions (at%) of Pt-14Al-3Re, Pt-14Al-4Ti, Pt-14Al-4Ta and Pt-14Al-4Cr were all characterised by a microstructure consisting of primary Pt₃Al surrounded by a fine two-phase eutectic-like mixture of a (platinum) matrix and fine particles of Pt₃Al. The proportion of primary Pt₃Al in Pt-14Al-4Ti, Pt-14Al-4Ta and Pt-14Al-4Cr alloys is between 40% and 50% and in Pt-14Al-3Re alloy it is about 25% according to optical microstructure analysis. The fine martensite-like lamellar structure was observed in Pt-14Al-3Re (Figure 4(a)) and Pt-22Al-2Ru (Figure 4(e)) alloys. This means the Pt₃Al phase has transformed from the high-temperature cubic structure (L₁₂) to the low-temperature tetragonal structure (D₀’c). In the Pt-14Al-4Ti and Pt-14Al-4Ta alloys, it seems that the high-temperature Pt₃Al phase is formed and maintained. This demonstrates that the third metal elements titanium and tantalum can stabilise the L₁₂ polymorph. It is important to observe that an alloying element must enter the Pt₃Al phase in order to prevent the low-temperature transformation of the Pt₃Al phase (55). Biggs (56) and Hill (57) have also shown the possibility for other alloy third components (nickel, titanium or chromium) in Pt-Al alloys to stabilise the cubic (L₁₂) structure of Pt₃Al.

Hill et al. (58) studied the microstructure and lattice mismatch of Pt-Al-X alloy systems with stabilising elements titanium, chromium, tantalum, ruthenium and iridium. Figure 5 shows TEM images of the typical two-phase microstructure. All the precipitated phases show a bimodal or even trimodal size distribution. Titanium, chromium and tantalum elements enter into the Pt₃Al phase to stabilise the cubic L₁₂ structure, the precipitation phase has a cubic appearance with no clearly discernible internal structure (Figure 5(a)). On
the contrary, when ruthenium and iridium enter the platinum matrix, the Pt₃Al precipitation phase transforms into a D₀’c structure, and presents a band-like structure with alternating light and dark distributions (Figure 5(b)). Under higher magnification, it was confirmed that the lamellar structure in the precipitation phase of the D₀’c tetragonal structure should belong to the twin structure (54).

The lattice misfits between the matrix and precipitate phase in the Pt-Al-X alloy system at room temperature and 800°C were measured respectively by XRD (58). The (220), (211) and (112) diffraction peaks are used to obtain the lattice constants of the platinum solid solution matrix, L₁₂-Pt₃Al and D₀’c-Pt₃Al precipitate phases, respectively (aₘ and aₚ represent the lattice constants of the platinum solid solution matrix and Pt₃Al precipitation phase, respectively). Then, the Lattice misfits δ between the precipitation phase and the matrix are calculated by Equation (i), and the results are listed in Table III. It can be seen that the degrees of mismatch for all alloys are negative and the difference in mismatch degrees at different temperatures is very small. Besides alloys containing ruthenium, the lattice misfit increases at high temperature and the cubic L₁₂ structure (alloys containing chromium, tantalum or titanium) has a lower degree of mismatch than the D₀’c structure (alloys containing iridium, ruthenium).

\[ \delta = 2 \left( \frac{a_{\text{ppt}} - a_{\text{matrix}}}{a_{\text{ppt}} + a_{\text{matrix}}} \right) \] (i)
3.2 Mechanical Properties of Ternary Alloys

Figure 6 shows the high-temperature compression strength of Pt-10Al-4Ru compared to Mar-M247 (a nickel-based superalloy) and the tensile strength of PM2000 (an iron-based superalloy) (22). It can be seen that the Pt-10Al-4Ru alloy based on γ/γ’ precipitation strengthening has higher compressive strength and the ability of withstand higher temperatures than the traditional nickel-based and iron-based superalloys at 1200°C.

Süss (59) studied the stress-rupture strength and high-temperature creep properties of the Pt-Al-X (X = chromium, ruthenium, iridium) ternary alloy system. Figure 7 shows the stress-rupture curves of Pt-10Al-4Ru and Pt-10Al-4Cr alloys at 1300°C. The alloys’ interpolated strength levels for a rupture time of 10 h are summarised in Table IV. PM2000 shows the highest high temperature rupture strength among all the tested alloys, but the lower slope of the stress-rupture curve indicates that the alloy has high stress sensitivity and brittle creep behaviour. This means PM2000 alloy is likely to be damaged by stress concentration or short-term overload in practical use. In contrast, the stress-rupture curve of platinum-based alloys has a steeper slope. Pt-10Al-4Cr alloy has the highest strength at 1300°C. The high-temperature durability of this precipitation strengthened alloy at 1300°C is higher than the ODS and DPH alloys (53) and the solid solution-strengthened Pt-20wt%Rh alloys, and is close to the strength of Pt-30wt%Rh alloys (10). However, due to wide price fluctuations of rhodium as well as processing difficulties, the practical application of Pt-30wt%Rh alloy is restricted (10).

### Table III Lattice Misfits Between Precipitates and Matrix for Selected Pt-Al-X Ternary Alloys (58)

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Pt₃Al type</th>
<th>Room temperature</th>
<th>800°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>aₘatrix, nm</td>
<td>a_ppt, nm</td>
</tr>
<tr>
<td>Pt-10Al-4Cr</td>
<td>L₁₂</td>
<td>3.9022</td>
<td>3.8741</td>
</tr>
<tr>
<td>Pt-10Al-4Ir</td>
<td>D₀°C</td>
<td>3.8983</td>
<td>3.8507</td>
</tr>
<tr>
<td>Pt-10Al-4Ru</td>
<td>D₀°C</td>
<td>3.9001</td>
<td>3.8530</td>
</tr>
<tr>
<td>Pt-10Al-4Ta</td>
<td>L₁₂</td>
<td>3.8941</td>
<td>3.8682</td>
</tr>
</tbody>
</table>

Fig. 6. High-temperature compression strength of Pt-10Al-4Ru alloy compared to Mar-M247 (a nickel-based superalloy) and the tensile strength of PM2000 (an iron-based superalloy) (22)

![Fig. 6. High-temperature compression strength of Pt-10Al-4Ru alloy compared to Mar-M247 (a nickel-based superalloy) and the tensile strength of PM2000 (an iron-based superalloy) (22)](image)

### Table IV Stress-Rupture Strength $R_m$ for PM2000 and Pt-10Al-4X Alloys (59)

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Stress rupture strength ($R_m/10$ h/$1300^\circ$C), MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM2000</td>
<td>25</td>
</tr>
<tr>
<td>Pt-10Al-4Cr</td>
<td>17</td>
</tr>
<tr>
<td>Pt-10Al-4Ru</td>
<td>15</td>
</tr>
<tr>
<td>Pt-10Al-4Ir</td>
<td>13</td>
</tr>
</tbody>
</table>

![Fig. 7. Stress-rupture curves of PM2000 and Pt-10Al-4X (X = chromium, ruthenium, iridium) alloys at 1300°C in air. Reprinted from (59), Copyright 2002, with permission from Elsevier](image)
Figure 8 shows the creep curves of the above alloys under the test conditions of 1300°C and 30 MPa (59). The initial stage of creep was not observed in the three platinum-based alloys. After the second-stage creep, the platinum-based alloys undergo the third stage of creep and subsequent rupture. The creep rupture strain was as high as approximately 10–30%. For PM2000 alloy, it is impossible to divide the creep curve into different stages because of the very low creep rate and fracture strain of less than 1%.

### 3.3 Oxidation Behaviour of Ternary Alloy

The service environment for components such as aeroplane engines, industrial gas turbine blades and aerospace engine thrusters is very harsh: high temperature, strong oxidation and corrosion. Although platinum-based superalloys with potential for high-temperature applications have been confirmed from the perspective of microstructure features and high-temperature mechanical properties, further attention must be given to assessing their oxidation and corrosion behaviour (10). Hill et al. (46) conducted oxidation tests on Pt-Al-Ni, Pt-Al-Ru, Pt-Al-Re, Pt-Nb-Ru and Pt-Ti-Ru in flowing air at 900°C, 1100°C, 1300°C and 1400°C, respectively. The study found that all aluminium-containing alloys show negligible weight loss on oxidation, while the Pt-Ti-Ru and Pt-Nb-Ru alloy systems have significant mass increases, indicating lower resistance to oxidation. Figure 9 shows optical micrographs of the transverse-sectional morphology of several platinum-based alloys (46). It can be seen that the Pt-Ti-Ru alloy has grain boundary oxidation, while severe internal oxidation has occurred in the Pt-Nb-Ru and Pt-Ta-Re alloys. The aluminium-containing alloy has formed a protective aluminium oxide film on its outer surface. This layer prevents oxidation of the underlying metal, conferring better oxidation resistance on this alloy.

Figure 10 shows the isothermal oxidation curves of aluminium-containing platinum-based ternary alloys Pt-10Al-4X (X = chromium, iridium, ruthenium, titanium) and PM2000 iron-based superalloys at 1350°C (10). It can be seen that Pt-10Al-4Ti and Pt-10Al-4Ru exhibit a parabolic oxidation law similar to the PM2000 alloy. The Pt-10Al-4Ir and Pt-10Al-4Cr alloys exhibit a parabolic change in the initial stage of oxidation, and the oxidation rate is relatively high. After that, the oxide film is grown at a logarithmic rate. After 800 h of oxidation a continuous oxide layer is obtained, which has better oxidation resistance than the PM2000 alloy. Experimental research on the microstructure, mechanical properties and oxidation resistance of the Pt-Al-X series of alloys...
superalloys and comparison with the PM2000 benchmark alloy leads to the conclusion that the highest performing platinum-based ternary superalloys are Pt-10Al-4Cr and Pt-10Al-4Ru (10).

4. Pt-Al-Cr-X Quaternary and Multi-Element Alloys

Early studies on platinum-based superalloys mainly focused on the addition of alloying elements to improve oxidation resistance and ensure the γ’ phase has a stable L1₂ structure. Research shows that the volume fraction of the precipitation phase reaches only about 30% no matter how the heat treatment process is optimised. Hence it is difficult to obtain the desired strength of the alloy (60). Subsequent work mainly focused on the Pt-Al-Cr ternary alloy system. Adding nickel, ruthenium and other alloying elements to form quaternary and multi-element platinum-based superalloys is expected to further improve the microstructure and to enhance the mechanical properties and oxidation resistance. Compared with steel, nickel-based alloys and aluminium alloys, the experimental data and phase diagrams of platinum-based alloys are relatively lacking. In order to develop quaternary and multi-element platinum-based alloys, relevant research institutions in South Africa, Germany and the UK have collaborated to establish Pt-Al-Ru (61) and Pt-Cr-Ru (62) ternary system and Pt-Al-Cr-Ni (63) quaternary system alloy databases by experiment and first-principles thermodynamic calculations.

4.1 Pt-Al-Cr-Ni Quaternary Alloy

Nickel has a good solid solution strengthening effect on the platinum matrix (64) and its addition can stabilise the L1₂ structure of the Pt₃Al phase. Researchers have added nickel to the Pt-Al-Cr alloy to form a Pt-Al-Cr-Ni quaternary alloy (36). In order to reflect the results of previous research on Pt-10Al-4Cr, the nominal composition ratio of Pt:Al:Cr in the quaternary alloy is designed to be approximately 86:11:3, and the maximum content of nickel is 10 at%. The Pt-11Al-3Cr-(0-10)Ni alloy system has a single-phase structure after solution treatment at 1450°C. The microstructure obtained is similar to that of nickel-based superalloys after ageing treatment at 1000°C, but alloys with nickel content below 6 at% seem to have a lower coherence of precipitation. After ageing treatment, the Pt-11Al-3Cr-6Ni alloy has a maximum γ’ phase volume fraction of about 23%. The cubic precipitate phase is arranged in a straight line with a side length of 200–500 nm, and the degree of mismatch between the precipitate phase and the matrix is about −0.1% (similar to nickel-based superalloys) (Figure 11). Spherical particles are observed in alloys with a nickel content of more than 6 at% and it is believed that the change in the γ’ phase morphology is due to the increase in the nickel concentration and a decrease in the degree of mismatch. Ageing at 1100°C will cause coarsening of γ’ phase and reduce the volume fraction of the γ’ phase. However, as ageing temperature increases, the volume fraction of the γ’ phase of the nickel-containing alloy decreases less than that of the nickel-free alloy. A Pt-(12-15)Al-3Cr-(4-8)Ni alloy with aluminium content near the solubility limit (15 at%) was selected to obtain a platinum-based alloy with high volume fraction of the γ’ phase (36, 37). For
alloys with aluminium content less than 13 at% it is possible to obtain a homogenised single-phase structure after heat treatment at 1500°C. Alloys with a higher aluminium content will form a eutectic two-phase dendritic structure even after heat treatment at 1530°C. For alloys with aluminium content less than 13 at%, ageing treatment at 120 h at 1000°C ageing produces a uniformly distributed precipitation of \( \text{Pt}_3\text{Al} \). Figure 12 shows cubic \( \text{Pt}_3\text{Al} \) particles with an average side length of 520 nm in the Pt-14Al-3Cr-6Ni alloy. The absolute mismatch between \( \gamma \) and \( \gamma' \) phases decreases with the increase of nickel content. For alloys with nickel content higher than 5 at%, the slightly negative mismatch value (less than \(-0.5\%\)) at room temperature and the cubic or spherical particle morphology of the \( \gamma' \) phase indicate that the \( \gamma \) and \( \gamma' \) phases are in a coherent state. Increasing the main \( \gamma' \) phase forming element (aluminium) to 13 at% can increase the volume fraction of \( \gamma' \) up to 30% (37).

![Fig. 12. SE image of Pt-14Al-3Cr-6Ni after solution heat treatment at 1500°C for 12 h and ageing at 1000°C for 120 h. Reprinted by permission from Springer Nature Customer Service Centre GmbH: Springer Nature, (37), Copyright (2005)](image)

The alloy system Pt-Al-Cr-Ni was studied with an aluminium content limited to 12.5 at% and a chromium content up to 6 at%. The effect of chromium content and heat treatment on the volume fraction of the \( \gamma' \) reinforcing phase is reported (34). Analysis of the microstructure showed that the dendritic cast structure of Pt-12.5Al-3Cr-6Ni, Pt-12Al-6Ni and Pt-12Al-6Cr-6Ni can be homogenised by heat treatment at 1500–1510°C. After homogenisation treatment (12 h at 1500°C), the \( \text{Pt}_3\text{Al} \) precipitation in the Pt-12.5Al-3Cr-6Ni alloy was almost completely suppressed after water quenching (Figure 13(a)). Air cooling causes the \( \text{Pt}_3\text{Al} \) particles (average size 200 nm) to be uniformly distributed with a volume fraction of about 30% (Figure 13(b)). Furnace cooling from 1500°C resulted in cubic and coarse particles distributed in the alloy with a volume fraction of 34% (Figure 13(c)). Increasing the chromium content to 6 at% resulted in \( \text{Pt}_3\text{Al} \) with an average particle size of 500 nm and a volume fraction that reached 50% after solution heat treatment for 6 h at 1500–1510°C and air cooling.

The \( \gamma' \) phase dissolves at very high temperatures, therefore the designed platinum-based superalloys have a maximum operating temperature of 1300°C. Figure 14 shows the stress-rupture strength curves of Pt-10wt%Rh, Pt-10wt%Rh DPH and Pt-12Al-6Cr-5Ni alloys at 1300°C (65). The latter has the highest fracture strength. The minimum creep rate of Pt-12Al-6Cr-5Ni alloy is almost three orders of magnitude lower than that of the initial Pt-10Al-4Cr alloy at 1300°C. Under the stress of 30 MPa, the creep performance of Pt-12Al-6Cr-5Ni alloy is better than the PM2000 benchmark alloy (Figure 15). Adding a small amount of boron (0.3 at% or 0.7 at%) can significantly improve the creep strength and ductility of the Pt-12Al-6Cr-5Ni

![Fig. 13. Secondary electron SEM micrographs of Pt-12.5Al-3Cr-6Ni after homogenisation for 12 h at 1500°C and different cooling regimes: (a) water quenched; (b) air cooled; (c) furnace cooled. Reprinted by permission from Springer Nature Customer Service Centre GmbH: Springer Nature, (34), Copyright (2004)](image)
alloy (66). To investigate the oxidation resistance of Pt-12Al-6Cr-5Ni, Wenderoth et al. (67) studied its isothermal oxidation behaviour of after 400 h exposure to a temperature range of 1100–1300°C in air. A layer of Al₂O₃ was observed on the surface below which a free γ'-free layer was detected. It was also observed that the size of the γ'-free layer continuously increases with time and temperature. Furthermore, the local concentration of aluminium in the γ'-free layer increases with elevated ageing temperatures. After 400 h exposure at 1300°C a thick polycrystalline Al₂O₃ scale with large oxide grains developed on the surface. This is in good agreement with the typical behaviour of alloy systems forming protective Al₂O₃ scales.

### 4.2 Pt-Al-Cr-Ru Quaternary Alloy

The strong solid solution strengthening element ruthenium can be added to the Pt-Al-Cr ternary alloy to form a Pt-Al-Cr-Ru quaternary alloy. This increases the volume fraction of the γ' phase and further improves the mechanical performance and oxidation resistance of the alloy (68). **Figure 16** shows the typical TEM two-phase microstructure of Pt-12Al-4Cr-2Ru (at%) alloy with the Pt₃Al precipitation phase and the (platinum) matrix (69). The volume fraction of the Pt₃Al precipitate has increased significantly, with the highest volume fraction of the precipitation phase in platinum-based alloys found so far. The morphology of the precipitation phase is mainly cubic with a side length of about 200 nm and a small amount being irregular. XRD analysis confirmed that the Pt₃Al precipitation phase is cubic.

The quaternary alloy was prepared by arc melting and then aged in air for 100 h at 1250°C in a muffle furnace. It was then water quenched. Test samples for investigation of mechanical properties were obtained from the bulk material by machining. **Table V** lists the mechanical properties of several Pt-Al alloys, iron-based (PM2000) and nickel-based (CMSX-4) superalloys (68). From the performance
comparison of the three platinum-based alloys, it can be found that the quaternary alloy has the highest hardness value, but its room temperature tensile strength and elongation are the lowest. This is inconsistent with the expected result of ruthenium as a strong solid solution strengthening element. The tensile fracture morphology of the alloy was analysed. It was found that only the Pt-11Al-3Cr-2Ru alloy showed intergranular fracture, while all the ternary alloys had cleavage fracture with some localised signs of dimpling. It is likely that the lower ultimate tensile strength value of the quaternary alloy is related to the intergranular failure mode, which also correlates to the lower plasticity expressed by the lower elongation value. Compared with iron-based and nickel-based superalloys, the tensile strength of platinum-based superalloys is within the ultimate tensile strength range of high-temperature alloys at room temperature.

Odusote (70, 71) studied the isothermal oxidation behaviour of Pt-11Al-3Cr-2Ru (at%) at 1350°C in air. It is found that the oxide layer of the alloy is mainly composed of α-Al₂O₃ and the thickness of the oxide layer increases with the oxidation time according to a parabolic law (similar to Pt-Al-Cr or Pt-Al-Ru alloys). The growth mechanism of the oxide layer is mainly the diffusion of oxygen atoms into the inner layer along the oxide grain boundary, accompanied by the outward diffusion of a small amount of aluminium atoms. The oxide protective layer is dense, has good adhesion to the substrate and no local discontinuities or detrimental internal oxidation phenomena have been found (Figure 17) (71). These characteristics of the oxide layer indicate that the Pt-11Al-3Cr-2Ru alloy has good oxidation resistance and has the potential for high-temperature applications.

Alloys belonging to the Pt-Al-Cr-Ru series are currently being developed since they show the best overall performance. However platinum-based alloys have the disadvantages of high price and high density (10). The addition of a cheap and low-density alloy element to replace part of the platinum while maintaining the high-temperature properties and desired microstructure is a subject of current research. Wenderoth et al. (72) added the refractory metal niobium to the platinum-based alloy to improve the high-temperature strength through precipitation hardening. Vanadium belongs to the same group of the Periodic Table as niobium but has a smaller atomic radius and higher solid solubility in the platinum matrix. As well as its effect on precipitation hardening, vanadium may also have a solid solution hardening effect. Odera et al. (73) prepared and analysed four Pt-Al-Cr-Ru-V five-component alloys and two Pt-Al-Cr-Ru-V-Nb six-component alloys by adding vanadium and niobium on the basis of a Pt-12Al-4Cr-2Ru quaternary alloy with excellent properties. Vanadium was added in the range 5.2–19.0 at%, niobium was added in smaller amounts. The content of platinum was reduced to the range 63.2–78.7 at%. The study found that the expected Pt₃Al precipitate appeared and that a two-phase structure (matrix with precipitates) was obtained in the four cast alloys, while two alloys had a single-phase structure with

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Hardness, HV</th>
<th>Ultimate tensile strength at room temperature, MPa</th>
<th>Elongation, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt-10Al-4Cr</td>
<td>317 ± 13</td>
<td>836</td>
<td>~4</td>
</tr>
<tr>
<td>Pt-10Al-4Ru</td>
<td>278 ± 14</td>
<td>814</td>
<td>~9</td>
</tr>
<tr>
<td>Pt-11Al-3Cr-2Ru</td>
<td>361 ± 10</td>
<td>722</td>
<td>~1</td>
</tr>
<tr>
<td>PM2000</td>
<td>–</td>
<td>700</td>
<td>14</td>
</tr>
<tr>
<td>CMSX-4</td>
<td>–</td>
<td>870</td>
<td>–</td>
</tr>
</tbody>
</table>

![Figure 17. SEM-SE cross-section image of Pt-11Al-3Cr-2Ru (at%) specimen after 100 h oxidation in air at 1350°C. Reprinted by permission from Springer Nature Customer Service Centre GmbH: Springer Nature, (71), Copyright (2012)](https://doi.org/10.1595/205651321X16221908118376)
vanadium preferentially distributed in the platinum matrix. The hardness of multi-element platinum-based alloys is higher than the quaternary alloys. The optimal vanadium content is about 15 at% to obtain the desired microstructure. A higher vanadium content leads to the formation of a brittle Pt-V mesophase. Niobium loss was too high for its alloying effect to be determined. According to the preliminary experimental results on microstructure and hardness of the multi-element systems based on platinum alloys, these materials have promise for high-temperature applications although further optimisation of their composition is necessary.

5. Research on Hot Corrosion Performance of Platinum-Based Superalloys

For materials used in high-temperature environments, the focus is usually on high-temperature strength (74). However, the creep, oxidation and corrosion resistance of alloys are also important (75). Increasing operating temperature will lead to continuous corrosion. Therefore, it is necessary to evaluate the corrosion resistance of high-temperature materials during the selection process (1, 76). For nickel-based superalloys, the high-temperature strength of the alloy is improved by increasing the content of aluminium and reducing the content of chromium, but the alloy is more sensitive to high-temperature corrosion, and it is necessary to develop and introduce protective coatings (77).

Since platinum-based alloys show excellent performance in various high-temperature applications such as glass manufacturing and corrosive substance processing, platinum-based alloys can be used to solve problems encountered in the aerospace industry (29, 78). Platinum-based superalloys are relatively new high-temperature materials, and there are very few literature reports on their corrosion properties. Fuel or intake air usually contains impurity elements such as sodium, sulfur and vanadium, which may form molten salt corrosion products such as Na₂SO₄, NaCl and V₂O₅, which in turn may lead to high temperature hot corrosion (HTHC) of materials (22, 79). Hot corrosion caused by molten salt or corrosive gas accelerates the oxidation degradation of high temperature materials, adversely affects the mechanical properties of the alloy and shortens the service life of high temperature components. There are two types of hot corrosion in nickel-based superalloys: Type I and Type II. Type I hot corrosion is also known as HTHC and usually occurs in the temperature range 850–950°C. Type II hot corrosion is also known as low temperature hot corrosion (LTHC) and generally occurs in the temperature range 650–800°C (79). Type I or HTHC is the main corrosive process in aircraft gas turbine engines.

Maledi et al. (80) studied the accelerated corrosion behaviour of five platinum-based superalloys in analytically pure anhydrous Na₂SO₄ at 950°C and compared them with NBSA with 1.25 μm thick Pt₃Al coating protection or no coating. The experimental results are listed in Table VI (76). The corrosion kinetics of nickel-based and platinum-based superalloys for the first 50 h are shown in Figure 18 and Figure 19, respectively. Due to the protective oxide layer formed on the surface of the platinum-based alloy, the weight gain associated with corrosion is very small. On the other hand, uncoated NBSA form oxides in the initial stage of corrosion, leading to increased mass. After further exposure to the corrosive environment, non-protective oxides form and cause catastrophic corrosion damage. Although the coated NBSA has better corrosion resistance than the uncoated alloy, it still degrades

<table>
<thead>
<tr>
<th>Table VI</th>
<th>Platinum-Based Superalloys and Nickel-Based Superalloys Together with their Corrosion Kinetics After Treatment in Na₂SO₄ at 950°C for 540 h (76)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy name</td>
<td>Nominal composition, at %</td>
</tr>
<tr>
<td>RS-1</td>
<td>Pt-10Al-4Cr</td>
</tr>
<tr>
<td>RS-2</td>
<td>Pt-10Al-4Ru</td>
</tr>
<tr>
<td>RS-3</td>
<td>Pt-11Al-3Cr-2Ru</td>
</tr>
<tr>
<td>P420</td>
<td>Pt-15Al-6Co</td>
</tr>
<tr>
<td>P421</td>
<td>Pt-15Al-12Co</td>
</tr>
<tr>
<td>CMSX-4 (uncoated)</td>
<td>Ni-6.5Cr-11Co-0.3Mo-1.7W-1.8Ta-11.3Al-0.9Ti</td>
</tr>
<tr>
<td>CMSX-4 (coated)</td>
<td>Ni-6.5Cr-11Co-0.3Mo-1.7W-1.8Ta-11.3Al-0.9Ti</td>
</tr>
</tbody>
</table>

© 2021 Johnson Matthey
prematurely compared to the platinum-based superalloy. Experiments show that in the molten Na₂SO₄ environment, platinum-based alloys show superior corrosion resistance compared to both coated and uncoated NBSA. Figure 20 shows the protective layer with strong adhesion formed on the surface of the Pt-10Al-4Cr alloy. The surface protective layer morphology of the Pt-10Al-4Ru and Pt-11Al-3Cr-2Ru alloys is similar (80). Although the morphology of the surface oxide layer of platinum-based superalloys containing chromium or ruthenium appears porous, their resistance to hot corrosion is higher than that of the platinum-based superalloys containing cobalt. NBSA was subjected to penetration of sulfur under the surface oxide layer, leading to formation of chromium and nickel sulfides. This alloy showed the worst resistance to sulfidation and hot corrosion. Resistance to sulfidation was also the subject of studies in the experimental work of Potgieter et al. (81). The results of the study are shown in Table VI. The tests were performed in a 0.2% SO₂-N₂ mixed atmosphere and research conclusions were similar to those obtained by Maledi et al. (80).

6. Conclusions

More than 20 years of research and development have yielded interesting results for platinum-based superalloys. The results obtained so far are only the tip of the iceberg of a very interesting and topical subject characterised by excellent prospects for future use. Optimised design of alloy composition, microstructure characteristics, mechanical properties and oxidation corrosion behaviour have been achieved. Among the systems studied so far, the Pt-Al-Cr-Ru alloy system has been selected and optimised for excellent performance. The ultimate goal is to develop platinum-based superalloys for application in industrial fields such as gas turbine engines. However, this is a competitive market that is difficult to penetrate with new materials. One possibility would be to exploit the possibility for platinum-based alloys to be used at temperatures 200°C higher than for NBSA (82). During the transition period, platinum-based superalloys could...
be used in other fields, such as castings, powder metallurgy products and coatings to accelerate their final use in gas turbine engines.

At present, the composition and structure design of platinum-based superalloys mainly follows the successful experience of NBSA development. The melting point of platinum is 316°C higher than that of nickel, but the difference in melting point between platinum-based superalloys and nickel-based superalloys is less than 150°C. The main reason for this discrepancy is the addition of low melting point alloying elements (such as aluminium) which reduces the melting point of the resulting alloy to about 1500°C. The advantage of platinum’s high melting point has thus not yet been fully exploited. The development cycle of a new generation of superalloys is very long and the material cost is relatively high for precious metals. The optimisation process for the design of new platinum-based superalloys could be accelerated with the help of material genome research concepts to further increase the alloy’s temperature tolerance and reduce research and development costs.

Platinum-based superalloys can still be considered a brand new alloy system when compared to, say, NBSA or stainless steels. The accumulation of fundamental data such as phase precipitation mechanisms and alloy properties is far from being complete. There has been little research on the influence of manufacturing processes (for example, precision casting, directional solidification and single crystal preparation) on the formability and mechanical properties of the alloys. There has similarly been insufficient verification and assessment of performance under actual use in typical environmental conditions. To accelerate bringing these materials to market, the level of research and development on platinum-based superalloys needs to be improved urgently.

Acknowledgments

This work is supported by Basic Research Key Program of Yunnan, China (No.2019FA048) and The Major Science and Technology Program of Yunnan, China (Nos. 2019ZE001, 202002AB080001-1).

References


The Authors

Professor Changyi Hu is the Director of the Research and Development Center of Kunming Institute of Precious Metals, China, as well as the Vice Director of State Key Laboratory of Advanced Technologies for Comprehensive Utilization of Platinum Metals, China. His research interests include alloys, films and coatings of platinum group metals, as well as work pieces of refractory metals for high-temperature applications.
Yan Wei is a Professor at Kunming Institute of Precious Metals, as well as the Head of High Temperature Materials Division at State Key Laboratory of Advanced Technologies for Comprehensive Utilization of Platinum Metals, China. Her main fields of research include alloys of platinum group metals, refractory metals and jewellery alloys.

Professor Hongzhong Cai is a Senior Researcher in the High Temperature Materials Division at Kunming Institute of Precious Metals, China. He is working on films or coatings of platinum group metals and high temperature ceramics, as well as structural materials of refractory metals prepared by chemical vapour deposition.

Li Chen is the Deputy Director of Kunming Institute of Precious Metals, China. He is a Principal Engineer of genome project of precious metal alloy materials in the Alloy Material Group, where he is working on first-principles calculations, database building of precious metal alloys and new high-temperature materials.

Xian Wang is a Researcher in the Research and Development Center of Kunming Institute of Precious Metals, China. He carries out modelling and simulation in computation materials science, and is currently working on finite element simulation and analysis, as well as database building of precious metal materials.

Xuxiang Zhang is a Chief Engineer in the High Temperature Materials Division at Kunming Institute of Precious Metals, China. His research experience includes platinum alloys and refractory metals for high-temperature use. He is now responsible for product structure design and quality analysis.
Guixue Zhang is a Principal Technician in the High Temperature Materials Division at Kunming Institute of Precious Metals, where he is in charge of the High Temperature Material Laboratory. He is mainly responsible for testing mechanical properties and analysing microstructures of high-temperature materials.

Xingqiang Wang is a Technician in the High Temperature Materials Division at Kunming Institute of Precious Metals, China. He is working on platinum alloys, refractory metals and titanium alloys, including the preparation of samples, parts fabrication and production.
Here, we report the frequency dependent ultrasonic attenuation of monometallic gold and bimetallic gold/platinum based aqueous nanofluids (NFs). The as-synthesised bimetallic NFs (BMNFs) revealed less resistance to ultrasonic waves compared to the monometallic NFs. Thermal conductivity of both NFs taken at different concentrations revealed substantial conductivity improvement when compared to the base fluid, although gold/platinum showed lesser improvement compared to gold. Characterisation of the as-synthesised nanoparticles (NPs) and fluids was carried out with X-ray diffraction (XRD), ultraviolet-visible (UV-vis) spectroscopy, transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDS). The distinct two-phase bimetallic nature of gold/platinum, its two plasmonic band optical absorption features and the spherical morphology of the particles were shown. The findings were correlated with the observed thermal and ultrasonic behaviour and proper rationalisation is provided. It
was revealed that the comparatively lesser thermal conductivity of gold/platinum had direct implication on its attenuation property. The findings could have important repercussions in both industrial applications and in the mechanistic approach towards the field of ultrasonic attenuation in NFs.

1. Introduction

Synthesis and analysis of metallic NPs having different configurations, properties, morphologies and sizes has attracted extensive interest in the research community (1–3). In recent years, much attention has been paid to the fabrication of colloidal bimetallic NPs (BMNPs) due to their superior catalytic, electric, magnetic and optical properties over monometallic NPs and a wide range of applications in sensors, catalysis, biomedical imaging, optochemical sensors, drug delivery systems and quantum dots (4–8). Incorporation of a second metal not only modifies physicochemical characteristics of their constituent parts but also offers novel characteristics because of synergistic interactions between the components (9). As a case in point, Singh et al. (10) studied the catalytic activity of bimetallic nickel-palladium NPs (Ni$_{0.60}$Pd$_{0.40}$) and found a high hydrogen selectivity (>80%) for the decomposition of hydrosy hydrazine at 323 K. The corresponding monometallic counterparts were either poorly active (nickel NPs) or inactive (palladium NPs). Feng et al. (11) observed significantly higher catalytic activity for the bimetallic gold/platinum nanodendrites towards oxidation of methanol when compared to the commercial platinum/carbon catalyst. They rationalised this result through enhanced electronic interaction among its constituents. Toupkanloo et al. (12) synthesised palladium/silver BMNPs by a conventional reduction method aided by sound waves and reported increased viscosity for ethylene glycol with the incorporation of the palladium/silver BMNPs. They also reported quite significant enhancement in the electrical conductivity of aqueous medium when incorporated with the above BMNPs and compared the data favourably with monometallic counterparts. Kumari et al. (13) fabricated gold/silver BMNPs using the juice of pomegranate fruit and reported enhanced catalytic activity and nitric oxide and hydroxyl radical scavenging activity by the bimetallic species. The enhanced properties of BMNPs make them good candidates for various industrial, research and medical applications. Thus, BMNPs have become a hot topic for researchers and scientists across various interests. Among the various bimetallic combinations being explored by contemporary researchers, the pairing of gold and platinum NPs appears very frequently. Gold NPs have a wide array of applications as a direct consequence of having a wide absorption band over the visible region in fields such as: molecular imaging in plasmonic photothermal therapy; organic photovoltaics; as a therapeutic agent in biomedical application; as sensory probes and in electronic conductors (14–16). An extremely important feature of gold NPs is the tunable optoelectronic property which can be tailored based on the size, morphology and aggregation rate of the particles (17, 18). Platinum NPs, on the other hand, have superior antioxidation and catalytic properties used in petrochemical cracking and electrocatalysis (19, 20). As a functional metal, platinum NPs, owing to their suitable Fermi level positioning and excellent electron interaction kinetics, can be utilised in hydrogen evolution and oxygen reduction reactions as an electrocatalyst (21). However, bimetallic gold/platinum NPs have shown impressive and in most instances superior performances in various applications compared to either of its constituents: gold and platinum (22–26).

Efforts have been devoted towards obtaining gold/platinum BMNPs with excellent optical, electronic and surface properties. For example, Bian et al. reported the synthesis of twinned gold-platinum core-shell star-shaped decahedra through epitaxial growth (23). Bao et al. reported the preparation of gold-platinum core–shell nanorods for in situ examination of catalytic reactions employing surface enhanced Raman scattering spectroscopy (24). Fang et al. reported the formation of gold/platinum hollow bipyramid frames by a simple mixing of the respective precursors (25). They reported that this configuration allows the excellent plasmonic property of the gold NPs to couple with the highly active catalytic sites of platinum, making it the ideal multifunctional platform for catalysing and monitoring reactions in real time. Yu and his group reported the fabrication of gold-platinum bimetallic alloy on palladium nanocubes for hydrogen peroxide oxidation (26). Their motivation was to balance the low hydrogen conversion of gold with the high hydrogen conversion ability of platinum and the low selectivity of platinum with the high selectivity of gold. They reported a much better hydrogen peroxide production for the bimetallic catalyst as a result of the carefully choreographed synergistic effects of gold and platinum. The growth of platinum NPs on gold nanoplates with excellent photoresponse has also been reported. Lou et al. reported the fabrication of anisotropic...
platinum loaded triangular gold nanoprisms as photocatalysts for hydrogen generation reaction (27). Zhang and Toshima have reported a simultaneous reduction method to prepare gold/platinum BMNPs for superior and stable catalytic activity in aerobic glucose oxidation (28). As gold-platinum BMNPs show a third order nonlinear phenomenon due to strong optical Kerr effect, it can be an excellent contender for the development of low dimensional gyroscopic systems (29).

Acoustic attenuation spectroscopy is a relatively new technique to characterise the stability and structure of semisolid topical delivery systems for cosmetic and pharmaceutical applications (30). Ultrasonic attenuation techniques have provided a new dimension to non-destructive testing (NDT) of highly sophisticated materials. It provides the particle size distribution (PSD) of suspended solid particles in a highly precise manner. Ultrasonic NDT offers material characterisation not only after fabrication but also during the processing of materials (31). High energy acoustic waves have been extensively used in both the industrial sector as well as in medical sciences. Controlling material characteristics by monitoring physical parameters such as structural inhomogeneity, elastic constants, thermal conductivity, phase transformation, size and dislocation that forecast potential use of the materials can be accomplished by determining frequency dependent ultrasonic absorption. Acoustic attenuation may also be utilised for extensional rheology determination (32, 33).

The past few decades have witnessed several research groups investigating the ultrasonic behaviour of aqueous solutions in search of a comprehensive mechanism so that better control over the procedure could be achieved (34–36). For fluidic suspensions, it has been found that in general microsized dispersants tend to lessen the wave propagation due to weak particle-liquid interaction whereas nanosized particles enhance the wave propagation due to increased particle-liquid interaction (34). NPs in fluids (known as NFs) present a fascinating case study for understanding the physical mechanisms governing the ultrasonic behaviour in liquid suspensions because of the wide varieties of manipulations that can be achieved by changing their compositions, concentrations or chemical nature. A decreased attenuation in NFs could lead to a better performance in ultrasound imaging techniques. Attenuation also affects the propagation of waves and signals in electrical circuits, optical fibres and in air, making this phenomenon a critical one in the fields of electrical engineering and telecommunications. It is thus imperative to develop fluidic systems with enhanced wave propagation or decreased attenuation properties that can account for a better performance in the above areas. Aqueous metallic NFs which are already heavily sought after due to their interesting plasmonic properties (30) could add value with impressive ultrasound properties. So far, only a handful of studies have been conducted on the ultrasonic properties of metallic NFs (30, 34). The combined study of ultrasonic and thermal properties and in particular effect of ultrasonic wave propagation on the thermal conductivity or vice versa for metallic NFs is, to the best of our knowledge, yet to be reported.

In this article we report the attenuation properties of gold monometallic and gold/platinum BMNFs. We observed that the attenuation property was lower in the BMNF compared to the monometallic one. We have also observed the thermal conductivity properties of both the NFs and have been able to rationalise our observation based on the physiochemical data at our disposal. A simple correlation between our observed attenuation and thermal conductivity properties combined with theoretical background provides us with the physical explanation for the decreased attenuation properties in the BMNF.

2. Materials and Methods

The precursors used in the synthesis of BMNFs were hydrogen tetrachloroaurate(III) trihydrate (HAuCl₄·3H₂O) and hexachloroplatinic(IV) acid hydrate (H₂PtCl₆·xH₂O) obtained from HiMedia Laboratories Pvt Ltd, India. Trisodium citrate (Na₃C₆H₅O₇) was purchased from Merck KGaA, Germany. The chemicals used were reagent grade and were used without further purification. The synthesis of the metallic NFs were conducted following previously reported procedure (37). Briefly, 0.1 wt% solution of HAuCl₄·3H₂O (10 ml) was stirred robustly and boiled. An aqueous solution of 1.0 wt% of Na₃C₆H₅O₇ (2 ml) was mixed in the above solution in a dropwise manner and was subsequently stirred for 5 min. The colour transformation from light yellow to vivid magenta after the addition of Na₃C₆H₅O₇ indicates the development of stable gold NF. For the preparation of BMNFs, 10 ml 0.1 wt% aqueous solution of H₂PtCl₆ was added to this NF followed by the further addition of 2 ml 1.0 wt% aqueous solution of Na₃C₆H₅O₇ with concomitant vigorous stirring; the entire solution being kept at room temperature. The final solution was heated.
up in a microwave oven in a cyclical on/off manner for 5 min (on 15 s, off 5 s). The cyclical process was accommodated to avoid extreme boiling and aggregation of the reaction components. The solution turned to greyish following the microwave treatment indicating the formation of gold/platinum BMNFs (35). The flowchart for the synthesis process of gold/platinum BMNFs has been presented in Figure 1.

The crystalline nature and phases of gold/platinum BMNPs were examined by X’Pert PRO diffractometer (PANalytical, The Netherlands) having monochromatic Cu-Kα radiation (λ = 1.5406 Å). NPs were drop cast on a cleaned glass substrate and the as-deposited thin films were utilised for the XRD technique. EDS and elemental analysis of gold NPs and gold/platinum BMNFs were done by the TEAM™ EDS analysis system with Octane Plus silicon drift detector (SDD) (EDAX Inc, USA). Microstructural morphology and reciprocal space analysis of the synthesised materials were conducted by the high-resolution TEM (HRTEM; Tecnai™G2 F30 S-TWIN, FEI Company, USA). Optical properties were evaluated using a LAMBDA™ 35 UV-vis spectrophotometer (PerkinElmer Inc, USA). PSD and frequency and concentration dependent ultrasonic attenuation at room temperature in both the NFs were determined by APS-100 acoustical particle sizer (Matec Applied Sciences, USA).

Thermal conductivities of gold NPs and gold/platinum BMNFs were determined by the Hot Disk TPS 500 Thermal Constants Analyser (Hot Disk AB, Sweden) which works on the principle of transient plane source (TPS) method. The TPS technique is the advanced version of transient hot wire (THW) technique. In this technique, Fourier’s law of heat conduction is used to measure the value of thermal conductivity of the subject materials. The technique corresponds to uncertainties of about 2%.

3. Results and Discussion

3.1 Structural Analysis, EDS Spectra and Elemental Mapping

Figure 2 shows the XRD pattern of bimetallic gold/platinum NFs. The pattern does not indicate gold-platinum alloy configurations but confirms the two phases: gold and platinum of the BMNPs individually. This may be due to the thermal immiscibility of gold and platinum at low temperature. The pattern shows diffraction peaks at 2θ = 38.52⁰, 44.23⁰, 64.06⁰ and 77.68⁰ corresponding to (hkl) planes (111), (200), (220) and (311) respectively of the face centred cubic (fcc) gold structure having a lattice constant of 4.078 Å (Joint Committee on Powder Diffraction Standards (JCPDS) No. 04-0784). Additional and relatively diminutive peaks obtained

---

**Fig. 1. Flow chart for synthesis of gold/platinum BMNFs**

**Fig. 2. XRD pattern of gold/platinum BMNFs**
at $2\theta = 39.72^\circ$ and $67.47^\circ$ correspond respectively to the $(hkl)$ planes (111) and (220) of the fcc crystal structure of platinum with a lattice constant of 3.923Å (JCPDS No. 04-0802). The average crystallite sizes ($D$) of the two phases of BMNPs have been calculated using the Scherrer equation (Equation (i)) (38):

$$D = \frac{0.9\lambda}{\beta\cos\theta} \quad (i)$$

where $\beta$ is full width at half maxima (FWHM) in radian, $\theta$ is the position of the peak in degrees, and $\lambda$ is the wavelength of X-ray. The average crystallite size for gold NPs and platinum NPs were calculated to be 19.4 nm and 31.3 nm respectively. This mathematical inference tallies well with the visual intuition obtained from the relatively wider diffraction peak of the gold NPs (Figure 2).

The elemental composition of the as-synthesised materials has been examined via EDS method (Figure 3). From the corresponding spectrum both gold and platinum were detected confirming the bimetallic nature of the sample. The atomic percentage was estimated to be Au:Pt $= 71.28:21.72$. Some extra peaks were also observed in the EDS spectrum corresponding to carbon and copper; the origin of which can be attributed to the carbon coated copper grid upon which the NFs were deposited for the EDS analysis. So, while calculating the atomic percentages these were ignored. The elemental mappings of the gold/platinum BMNFs are shown by Figures 4. Figures 4(a) and 4(b) show the independent distribution of gold and platinum NPs respectively while Figure 4(c) reveals the distribution of gold and platinum taken together in gold/platinum BMNFs. As was observed from the images, both the metallic particles were homogeneously distributed within the experimental range; however, the
concentration of gold NPs was clearly denser as compared to the platinum NPs, an observation that vindicates the findings of the EDS spectrum.

3.2 Particle Size Distribution and Microstructural Analysis

Microstructural analysis and the size distribution of the as-synthesised BMNF were carried out through TEM images. Figure 5(a) provides a collection of closely spaced gold/platinum bimetallic NPs. A more magnified view of the image reveals the almost spherical nature of the particles (Figure 5(b)). The distortion in the spherical morphology is slight and sometimes leads to the appearance of semi-ellipsoidal particle shape. Particle sizes estimated from a large group of particles such as observed in Figure 5(a) indicated that almost all the particles conform to such spherical/spheroidal morphology with average particle size staying within the range of 15–30 nm. Figure 5(c) displays the high resolution TEM micrograph of a single particle. Clear visible lattice fringes were indexed and the lattice planes matched well with the gold (200; \(d\) spacing = 0.204 nm, JCPDS - 04-0784) and platinum (111; \(d\) spacing = 0.231 nm, JCPDS - 04-0802) fcc crystal, indicating the simultaneous presence of gold and platinum lattice within the particle and confirming its bimetallic nature. The selected area electron diffraction (SAED) pattern is used to describe crystallinity of the NPs and is shown in the Figure 5(d). The unblemished ring pattern observed indicates the polycrystalline nature of the bimetallic particles which is well in agreement with observations from the XRD patterns (Figure 2).

PSD of NPs in both gold monometallic and gold/platinum BMNFs was studied by APS-100 acoustic particle sizer. This analysis method provides a PSD without any prior knowledge of the shape of the particles or even if the solution is concentrated. The APS-100 obtains the PSD data from the acoustic attenuation spectroscopy measurements. Usually as sound travels through a colloidal medium, it gets attenuated and this level of attenuation is related to the corresponding particle size within the colloidal solution. The as-obtained normalised PSD curves for both the monometallic gold and bimetallic gold/platinum NFs are displayed in Figure 6.

An interesting observation here is that particles in BMNFs are slightly larger in size compared to that of monometallic NFs. The reason for this may be the larger crystallite sizes of platinum zones as observed from the XRD pattern, leading to an enhancement of the particle sizes when the platinum crystallites are incorporated. The size distribution of NPs in gold/platinum BMNFs is wider when compared to that of the monometallic gold NFs. Overall, the size of the dispersed NPs was found to be in the range of 19 nm to 30 nm.
for the gold NFs and 22 nm to 36 nm for the gold/platinum BMNFs. The maximum distribution is found at ~23 nm for the monometallic and at ~27 nm for the bimetallic NPs. The obtained particle size range is slightly larger from that observed in the TEM micrograph (Figure 5), which could be due to the localised nature of TEM analysis or simply because of the variation observed as a consequence of the difference between a direct optical method and an indirect acoustic method of determination.

### 3.3 Optical Characteristics and Surface Plasmon Resonance Band Nature

UV-vis absorption spectroscopy was carried out to analyse the band structure of the metallic samples and to further confirm the formation of the gold monometallic and the gold/platinum bimetallic NPs. Figure 7 shows the absorption spectra of the bimetallic gold/platinum and monometallic gold NFs. Gold NPs of spherical nature usually display surface plasmon resonance (SPR) absorption band at ~520 nm which can be shifted depending on the size, shape and environment of the particles (39, 40). The absorption peak of gold NF was obtained at 529 nm and the slight red shift could have been a result of the less than perfect spherical shape of the particles as observed from the TEM micrographs (Figure 5). The absorption peak of the gold/platinum BMNF is obtained at 542 nm indicating the dominance of gold NP in the overall absorbance feature of the bimetallic species. It also confirms the surface disposition of the gold NPs alongside platinum. Otherwise, platinum would have overwhelmed the SPR characteristics of gold and a featureless absorbance spectrum could have been obtained, as is usually observed for platinum in the visible region. The reason for apparent red shift (529 nm → 542 nm) could be an increased asymmetry in the shape of the gold NPs. But since the gold has been synthesised beforehand, that scenario should be ignored, as platinum particles affecting the shape of the gold NPs is pretty unlikely. No alloying was detected in the XRD pattern of the particles and so shifting due to alloying is also unlikely. So, the only possible reason for the shifting could be the change of the dielectric environment of the gold NPs due to the presence of platinum around them. The other broad absorption peak observed at 634 nm for the bimetallic gold/platinum NF could be attributed to the relative aggregation of gold NPs due to slight decrease in its surface charge as a result of platinum incorporation. The aggregation would lead to dielectric coupling between the particles leading to a broad absorption band north of 600 nm (41). The shifting in the SPR band in the visible region indicates the possible use of the BMNFs in the fabrication of optochemical sensors and as an effective photocatalyst (42, 43).

### 3.4 Ultrasonic Attenuation and Thermal Conductivity

Frequency and concentration dependent ultrasonic attenuation were measured in monometallic and BMNFs at room temperature and the obtained
results are provided in Figure 8. Evidently, the attenuation in both the NFs increases with increasing frequency. The increment is almost linear up to a certain frequency range beyond which it accelerates faster and the relationship apparently becomes non-linear. Sound waves become more attenuated in the NFs as compared to pure water. Furthermore, it is clear that attenuation is lower in the BMNFs than monometallic gold NFs.

Ultrasonic attenuation is highly sensitive to the local environment of the medium (44–46). Here, the macroscopic interfaces of mono and bimetallic NPs with water molecules become a vital factor to regulate their final values. The effective sound absorption by NPs in base matrix suspensions may be stated as Equation (ii):

$$\alpha = \alpha_m + \alpha_b + \alpha_{nb}$$

where $\alpha_m$ is the attenuation due to metal NPs, $\alpha_b$ is the corresponding part of absorption due to the base matrix and $\alpha_{nb}$ is the modification to the final value of $\alpha$ due to the interaction between metal NPs and base-fluids molecules in conjunction with modified thermomechanical characteristics of nanocolloidal suspensions (47).

The characteristic absorption of the sound wave due to individual particles is usually insignificant (48, 49). Existence of a stable interface between NP and base matrix molecules plays a significant role in determining the value of $\alpha_{nb}$. Factors affecting attenuation properties for different particle-fluid combinations have been explored previously. Kor et al. (50) investigated ultrasonic attenuation in gold due to phonon-phonon interaction, electron phonon interaction and thermoelastic loss. They reported total ultrasonic attenuation $\sim 3$ dB cm$^{-1}$ along $\langle 100 \rangle$ direction and $\sim 6$ dB cm$^{-1}$ along $\langle 110 \rangle$ direction. So, the nature of the facets plays an important role in determining the extent of attenuation. In general, the total sound attenuation in the NP-liquid suspensions depends upon scattering loss, viscous loss and thermal loss (51, 52). Biwa et al. (53) investigated the sound attenuation in liquid suspensions having millimetre sized particles using a differential scheme. They reported significant particle-reinforced attenuation due to scattering of the wave. But in case of colloidal dispersions or for nanosized particles, the particle sizes are usually smaller than the sound wavelength and as a result dissipative process rather than the scattering process govern the acoustical behaviour of such systems (54). So, for the time being it may be assumed that viscous loss and thermal loss are to play major roles in determining the acoustical properties of the present NF systems.

The expressions for thermal wavelength ($\Lambda_T$) and viscous wavelength ($\Lambda_v$) (Equations (iii) and (iv)) (55):

$$\Lambda_T = \sqrt{2K/(\rho C)}$$ (iii)

$$\Lambda_V = \sqrt{2\eta/(\rho \omega)}$$ (iv)

where $K$, $\rho$ and $C$ are thermal conductivity, density and specific heat of the suspended particles and $\omega$ is the frequency of the sound wave.

where $\eta$ is the viscosity of the base fluid.

In the present case, calculated values of $\Lambda_T$ and $\Lambda_V$ are of the order of $10^{-6}$ m and $10^{-7}$ m respectively for 10 MHz frequency which is not comparable to the size of the suspended metallic NPs. Thus, attenuation due to the viscous loss and thermal loss can be treated as insignificant. So, the behaviour of the whole curve can be explained in terms of effective attenuation due to interaction between acoustic phonon and lattice phonon of dispersed crystal in conjunction with Brownian motion induced enhanced thermal conductivity (K) of the NFs. The calculated value of thermal relaxation time for gold crystal is of the order of $10^{-10}$ s (50). The condition $\omega t << 1$ is maintained for the frequency range of 10 MHz to 100 MHz for the determination of effective attenuation which is directly proportional to thermal relaxation time ($\tau$) Equation (v):

$$\tau = 3 K/(C_v \bar{V}^2)$$ (v)

where $C_v$ denotes specific heat per unit volume and $\bar{V}$ denotes Debye average velocity. Thus, it may be assumed that the attenuation in the NFs is directly proportional to their individual thermal conductivity.

These results of the gold/platinum BMNFs may be confronted with recent developments in the field of ultrasonic studies of similar type of BMNFs. Hurtado-Aviles et al. (29) observed strong influence of ultrasonic waves on the optical and plasmonic properties of ethanol-based gold-platinum BMNFs which is very effective for instrumentation and low-dimensional signal processing.

Figure 9 displays concentration dependent thermal conductivity of the monometallic and BMNFs at room temperature. It indicates that thermal conductivity of both the NFs increases with NPs loading. Another notable observation is that the conductivity is consistently lower in the bimetallic species as compared to the monometallic species. At room temperature (27°C) and at 0.05 wt% concentration the thermal conductivity of the
gold NF and the gold/platinum BMNF was found to be 0.75 W mK\(^{-1}\) and 0.7 W mK\(^{-1}\) respectively or having a ratio of \(K_{\text{bi}}/K_{\text{mono}} = 0.93\). At 0.2 wt% the thermal conductivity of gold NFs and gold/platinum BMNFs were estimated to 1.12 W mK\(^{-1}\) and 0.99 W mK\(^{-1}\) respectively i.e., having a ratio of 0.88. So, with increasing concentration the thermal conductivity of the monometallic NF enhances at a slightly faster rate compared to that of the gold/platinum BMNFs. So, the present observation of the ultrasonic attenuation being lower in the BMNF can be rationalised from the comparative thermal conductivity behaviour of the two NFs.

There is no specific model for explaining the thermal conductivity behaviour of BMNFs. Most of the traditionally utilised models for composite materials such as Maxwell-Garnett do not properly explain the enhancement in NFs where nanosized particles have direct interfacial interactions with the matrix; fluid in this case (56). A subsequent model proposed by Kumar et al. (57) was somewhat appropriate in rationalising the thermal conductivity behaviour of the NFs. They incorporated the idea of parallel thermal conductivity between the NPs and the liquid particles. They explained the variation of thermal conductivity in the NF with temperature as being due to the variation in particle velocity with temperature. Subsequent researchers have proposed that the Brownian motion of the particles intensifies in the NF with increased temperature and volume fraction of the NPs in base fluid, while its effects diminish with increasing particle size (57, 58). Kumar et al. in their paper also countered the argument of interfacial resistance in such systems by proposing that the surface interaction is facilitated by the larger specific surface area of the nanosized particles (57). According to their proposed model, the expression for thermal conductivity of NP-liquid suspensions could be explained by Equation (vi): 

\[
k = k_f \left[1 + \frac{\phi k_{np}}{k_f (1 - \phi) r_n}\right]
\]

where \(k\) is thermal conductivity of the NF and the subscripts \(f\) and \(n\) represent base fluid and NP respectively. It is obvious from the above equation, that thermal conductivity enhancement is linearly proportional to concentration of NPs (\(\Phi\)) and inversely proportional to the radius (\(r\)) of the NPs. Significant enhancement in thermal conductivity at small concentration of the suspended NPs can be described using this model.

Past research on gold/platinum systems has shown that the thermal conductivity of the solid system depends on its composition (59). Metallic gold has significantly higher thermal conductivity compared to metallic platinum. At a lower percentage of gold, the system could potentially be occupied by individual single metallic phases and understandably, the thermal conductivity of that system, being an average of its components, would be lower as compared to pure gold solid system. Prior literature reveals that gold/platinum system could potentially start to form an alloy at the composition of about 70 at% gold, following which the thermal conductivity of the solid system could rise again (59). But the thermal conductivity of the system always stays well below that of single-phase gold. This would explain why the present gold/platinum nanoparticulate system would have a thermal conductivity lower than the gold NP system and in turn, would explain the lower thermal conductivity of the BMNF system compared to the gold monometallic system. Additionally, as observed from the APS-100 measurements, the average particle sizes of gold NPs are slightly lower than that of the average particle sizes of platinum. The smaller particle size of gold could mean a higher thermal conductivity and consequently a higher enhancement of thermal conductivity for the gold NF compared to the gold/platinum BMNF. Of course, as mentioned before, the exact mechanisms for the thermal conductivity within a NF is still not understood. It could be either of the above factors individually or a combination between the two that results in the lower thermal conductivity of the bimetallic moiety.

Thus, the reduced thermal conductivity in gold/platinum NFs in turn reduces sound attenuation
in gold/platinum NFs. As already explained, the attenuation property can be directly proportional to the NFs thermal conductivity, thus a reduction in the NF thermal conductivity results in loss of attenuation capability. The above results of ultrasonic studies of gold/platinum BMNFs should prove to be of significant implications in various industrial applications such as ultrasound imaging, extensional rheology, optochemical sensors, petrochemical cracking and therapeutic agents in the biomedical field.

4. Conclusions

Gold monometallic and gold/platinum BMNFs were synthesised via a simple microwave induced citrate reduction. The NFs were characterised in detail via various methods such as XRD which revealed a distinct two-phase bimetallic crystal structure without any alloy formation and by UV-vis which revealed the presence of two plasmonic bands in the bimetallic species with a tendency for aggregation. The elemental analysis further confirmed a bimetallic nature of the gold/platinum NFs. High resolution microscopy study revealed spherical NPs within the size range of 15–30 nm with well delineated lattice spacings belonging to both gold and platinum. The APS-100 studies revealed that the bimetallic NPs were of slightly larger particle size when compared to the monometallic ones. The ultrasonic characteristics of both the NFs were studied in conjunction with their thermal behaviour. The attenuation studies revealed that the BMNF has reduced attenuation when compared to the monometallic NF. The thermal studies conducted revealed that both the NFs had enhanced thermal conductivity compared to the base fluid which in this case was water. The gold/platinum NF was revealed to have slightly lower thermal conductivity compared to gold, which could be explained by its mixed metallic structure where platinum with a much lower thermal conductivity reduces the overall thermal conductivity of the bimetallic species. The lower thermal conductivity could perfectly explain the lower attenuation of the BMNF as previous studies had revealed that thermal conductivity is proportional to ultrasonic attenuation. The finding that gold/platinum BMNF could have lower attenuation as a result of lower thermal conductivity compared to monometallic gold NF can have significant repercussions in varied fields such as ultrasound imaging, extensional rheology and optochemical sensors.

Acknowledgments

Navneet Yadav acknowledges the financial support provided by the University Grants Commission, India.

References

21. L. Ma, S.-J. Ding and D.-J. Yang, Dalt. Trans., 2018, 47, (47), 16969
27. Z. Lou, M. Fujtsuka and T. Majima, ACS Nano, 2016, 10, (6), 5299
42. B. Karthikeyan and M. Murugavelu, Sensors Actuators B: Chem., 2012, 163, (1), 216
46. A. Sepehrinezhad and V. Toufigh, Ultrasonics, 2018, 89, 195
49. P. Awasthi, PhD Thesis, University of Allahabad, Old Katra, India, 2005

The Authors

Alok Kumar Verma is currently working as Assistant Professor in the Department of Physics, Prof. Rajendra Singh (Rajju Bhaiya) Institute of Physical Sciences for Study and Research, V.B.S. Purvanchal University, Jaunpur, India. He received his PhD degree in Physics from Department of Physics, University of Allahabad, India. His area of specialisation comprises optical, ultrasonic and thermal characterisation of nanostructured and thermoelectric materials for advanced applications. His research interests also include particles with superluminal velocity.
Navneet Yadav obtained his MSc in Physics with Spectroscopy and recently obtained PhD in Physics from the University of Allahabad, India. His research interests are in synthesis and characterisation of noble metals for antibacterial, anticancer, heat transfer and sensing applications.

Shakti Pratap Singh obtained his MSc in Physics with Spectroscopy and received his PhD degree from the Physics Department, University of Allahabad, India, in the field of Ultrasonics and Materials Science. He is currently working as Postdoctoral Fellow in the Department of Physics, Prof. Rajendra Singh (Rajju Bhaiya) Institute of Physical Sciences for Study and Research, Veer Bahadur Singh Purvanchal University, Jaunpur, India. His research interests are in the field of thermal and ultrasonic non-destructive characterisation of advanced materials for industrial applications.

Kajal Kumar Dey is currently serving as a Scientist/Assistant Professor and Head of Department at the Centre for Nanoscience and Technology of the Professor Rajendra Singh Institute of VBS Purvanchal University, Jaunpur, India. He did his doctoral research at the National Physical Laboratory (NPL), New Delhi in collaboration with the department of Physics, University of Allahabad. He worked as a SERB National Postdoctoral Fellow at the department of Chemistry of Indian Institute of Technology, Delhi. His research interests include catalysts and electrodes for water splitting reactions, the application of nanomaterials in antibacterial technology, gas sensing and coolant materials.

Devraj Singh is Professor in Department of Physics and Director of the Prof. Rajendra Singh (Rajju Bhaiya) Institute of Physical Sciences for Study and Research, Veer Bahadur Singh Purvanchal University, Jaunpur, India. He obtained his DPhil in Science at the University of Allahabad in 2002. His research and publication interests include the mechanical, thermophysical and ultrasonic characterisation of condensed and advanced materials. He is a Fellow of the Ultrasonic Society of India and a life member of a number of scientific societies. He has 91 research articles published in national and international journals of ultrasonic and materials science and 24 published books to his credit.

Professor Raja Ram Yadav is Ex-Vice-Chancellor VBS Purvanchal University and Professor of Physics at the Department of Physics, University of Allahabad. His research interests are in the non-destructive ultrasonic and thermal characterisation of nanomaterials, lyotropic liquid crystalline materials, intermetallics and semiconductors; the development of nanomaterials for biomedical applications; and theoretical calculations of nonlinear elastic and ultrasonic properties of crystalline materials. Professor Yadav successfully coupled ultrasonics with nanoscience and technology recognised as the new area of ‘Ultrasonics in Nanoparticles-Liquid Suspensions’ in the field of acoustics. He has 140 research articles.
It is known that platinum-rhodium thermocouples exhibit mass loss when in the presence of oxygen at high temperatures due to the formation of volatile oxides of platinum and rhodium. The mass losses of platinum, Pt-6%Rh and Pt-30%Rh wires, commonly used for thermocouples, were considered in this paper to characterise the mass loss of wires of the three compositions due to formation and evaporation of the oxides PtO₂ and RhO₂ under the conditions that would be seen by thermocouples used at high temperature. For the tests, the wires were placed in thin alumina tubes to emulate the thermocouple format, and the measurements were performed in air at a temperature of 1324°C, i.e. with oxygen partial pressure of 21.3 kPa. It was found that the mass loss of the three wires increases linearly with elapsed time, consistent with other investigations, up to an elapsed time of about 150 h, but after that, a marked acceleration of the mass loss is observed. Remarkably, previous high precision studies have shown that a crossover after about 150 h at 1324°C is also observed in the thermoelectric drift of a wide range of platinum-rhodium thermocouples, and the current results are compared with those studies. The mass loss was greatest for Pt-30%Rh, followed by Pt6%Rh, then platinum.

Introduction

Platinum-rhodium thermocouples are used widely as temperature sensors (1) and are often used in industry where the accuracy and stability requirements are greater than those that can be provided by less expensive base metal thermocouples. Examples of such processes are iron and steel manufacturing (2), quartz glass manufacturing and aerospace heat treatment and casting. Platinum and rhodium are also important industrial catalysts, for example for the oxidation of ammonia to nitric oxide (3, 4).

At temperatures above about 1200°C, it is known that platinum-rhodium thermocouple wires form volatile oxides where the solid platinum or rhodium oxide films formed on the surface of the wires at lower temperatures evaporate (5). This causes the wires to lose mass (3, 6–8), which is the dominant cause of progressive instability and thermoelectric inhomogeneity of the platinum-rhodium alloyed thermocouples. This instability arises because the vapour pressures and oxidation rates of platinum and rhodium are different. The overall behaviour also differs for each alloy (2, 6, 9). The departure of platinum and rhodium oxides from the wire at different rates causes a change in the composition of the thermoelements (4, 6) and hence calibration drift of the thermocouple.

An investigation conducted by Rubel et al. (4) studied the contribution of the volatile oxides to the mass loss of Pt-5%Rh and Pt-10%Rh alloy gauzes. The gauzes were exposed to oxygen over periods of 70 h to 300 h at 890°C and 1100°C. By using X-ray photoelectron spectroscopy (XPS), the type of volatile oxides produced were identified as platinum and rhodium oxides PtO₂ and RhO₂ respectively. It was also found that the rate of mass loss of rhodium oxide was greater with increasing rhodium content of the platinum-rhodium alloy.

Although the oxidation rates of platinum-rhodium alloys have not been investigated much in recent years, the effect of oxidation of the platinum group metals at high temperatures has been
widely studied. Phillips, in particular, studied the mass loss of the platinum group metals osmium, palladium, ruthenium, platinum, iridium and rhodium, and evaluated the time dependence of the mass loss by considering metal powders placed in 1” billets over the temperature range from 600°C to 1400°C (10). He concluded that all the platinum group metals lost mass when oxidised in air and that the rate of mass loss was greater at higher temperatures. Notably, the rate of mass loss increased with temperature, and for a given temperature the mass loss was linear with elapsed time, provided the volatile oxides are formed from the corresponding metal.

Another key experiment to determine the mass loss of platinum metals was conducted by Crookes (11). The two temperatures considered in that investigation were 900°C and 1300°C. The mass loss was investigated by using crucibles made of platinum and rhodium, where the original mass of platinum and rhodium was about 150 g and 33 g respectively. The mass loss was measured at time intervals of 2 h for a total period of 30 h. The significance of the results from this investigation was that at 900°C the mass loss of the platinum and rhodium crucibles was found to be negligible. However, at 1300°C it was found that the mass loss of both platinum and rhodium increased linearly with time. This measurement showed that volatile oxides are formed and vaporise at high temperatures, and that these are formed above some threshold temperature (3, 11).

Jehn (5) also observed a linear dependence of the mass loss with elapsed time, though it was noted in that study that in other experiments extended over “extremely long time periods” a marked increase in the mass loss rate had been observed for platinum at 1300°C after about 60 h (12) and 400 h (13); no explanation was given.

One difficulty with previous measurements of the rate of mass loss of platinum and platinum-rhodium alloys is the very wide dispersion of results, which vary by several orders of magnitude. This may be due in part to the wide variation of geometries of the test conditions, and the wide variation of environments (such as ambient gas or vacuum). Furthermore, none are applicable to typical thermocouple formats, which comprise thin noble metal wires inserted in narrow ceramic (typically alumina) bores. In addition, no attempt has been made to link the rate of mass loss of the wires to thermocouple drift performance. The aim of the current investigation was to perform such mass loss measurements in a manner that is directly applicable to thermocouples, to better inform thermocouple drift models based on evaporation of platinum and rhodium oxides. Wires of Pt-30%Rh, Pt-6%Rh and platinum were investigated in ambient atmospheric conditions, within a typical alumina insulation tube used for thermocouples to make the test as realistic as possible in the context of thermocouple usage. A temperature of 1324°C was selected for the tests, because this is the melting temperature of the cobalt-carbon alloy, which is a well-established temperature reference point (a so-called ‘fixed point’) for calibrating thermocouples, and is used for in situ periodic calibration during long-term experimental thermolectric drift tests.

In this article, the method is described, followed by a presentation of the results and an assessment of the associated uncertainties. The results are compared with thermocouple stability measurements where there are some intriguing qualitative similarities. Finally, some conclusions are drawn.

**Method**

Two identical wires were used for each type of wire to investigate the change of mass, where one wire was used as the control (kept at room temperature) and the other was the test wire exposed to high temperatures. This allows the change in mass to be calculated by comparing the masses of both wires. Measuring the mass change in this way reduces the influence of calibration drift and scale linearity of the mass balance. The wire diameter for all wires was 0.5 mm. The length of the platinum wire was 60 cm, while the Pt-6%Rh and Pt-30%Rh wires were 70 cm long.

Each of the wires was thoroughly cleaned using acetone and distilled water in order to remove any surface contamination prior to making mass measurements and heating. The wire masses were then measured using a Sartorius Supermicro S4 balance (Sartorius AG, Germany) with a resolution of 0.1 μg and a standard deviation of less than 1 μg. The measurement uncertainty of the mass comparison performed was approximately ±25 μg, largely due to random fluctuations in the readings. The balance was placed in a laboratory at a constant temperature (20°C ± 1°C), and the apparatus was kept in an isothermal enclosure to prevent the air from the surroundings from interfering with the measurements.

Prior measurements were made to determine how the surroundings affect the mass measurements using two scrap platinum wires. One wire was kept
as a control, where the scales were tared, and the other was the test wire (which in subsequent measurements would be the one exposed to high temperatures). The air conditioning in the laboratory caused short-term temperature fluctuations and air currents which manifested as long stabilisation times and noise in the mass measurements, so the thermal isolation of the balance was progressively improved until the stabilisation time and random fluctuations were both minimised.

To facilitate measurement on the balance pan, the wire was coiled around a plastic former to minimise contamination of the surface; the former was removed before weighing. Mass measurements of the test wires were made by comparison with the corresponding control wire, which was used to tare the balance. The mass of the control and test wires was measured three times to determine the average mass and to account for, and characterise, the random fluctuations in the test readings.

For each type of test wire used, three single alumina tubes of length 40 cm and diameter 3 mm, with bore diameter approximately 1 mm, were used. The wire was threaded into the bore to emulate the thermocouple format. The assembly was then placed in a thermal annealing furnace, which was maintained at 1324°C with stability of approximately ±1°C. Before beginning the experiment, the alumina tubes were maintained at 1500°C in air for 6 h to drive off volatile impurities, in order to minimise contamination of the test wires.

Results

The uncertainty of the mass measurements was assessed by considering the individual contributions listed in Table I, which were summed in quadrature in a manner consistent with the International Organization for Standardization (ISO) Guide to the Expression of Uncertainty in Measurement (GUM) (14). The two statistical contributions, i.e. repeatability and reproducibility, were assessed by considering the standard deviation of repeated weighings in situ and of re-weighing the same item (i.e. removing from the balance and replacing) several times. The resolution, accuracy of the weights used to calibrate the balance, linearity and temperature of the balance reading were obtained from the manufacturer’s specifications. For general applicability of the results, the mass loss was expressed per unit surface area (mg cm⁻²); this was determined by dividing the mass loss values by the surface area of the wires. This yields

<table>
<thead>
<tr>
<th>Description</th>
<th>Estimate, mg</th>
<th>Probability Distribution</th>
<th>Divisor, mg</th>
<th>Standard uncertainty, mg</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Repeatability</td>
<td>0.0064</td>
<td>Normal</td>
<td>1.0000</td>
<td>0.0064</td>
<td>Highest recorded value</td>
</tr>
<tr>
<td>Reproducibility</td>
<td>0.0039</td>
<td>Normal</td>
<td>1.0000</td>
<td>0.0039</td>
<td>Highest recorded value</td>
</tr>
<tr>
<td>Resolution</td>
<td>0.0001</td>
<td>Rectangular</td>
<td>1.7321</td>
<td>0.0001</td>
<td>From specifications</td>
</tr>
<tr>
<td>Accuracy of calibration weights</td>
<td>0.0100</td>
<td>Normal</td>
<td>1.0000</td>
<td>0.0100</td>
<td>From specifications</td>
</tr>
<tr>
<td>Linearity</td>
<td>0.0003</td>
<td>Rectangular</td>
<td>1.7321</td>
<td>0.0002</td>
<td>From specifications</td>
</tr>
<tr>
<td>Temperature dependence</td>
<td>0.0002</td>
<td>Rectangular</td>
<td>1.7321</td>
<td>0.0001</td>
<td>From specifications</td>
</tr>
<tr>
<td>Combined uncertainty</td>
<td>-</td>
<td>Normal</td>
<td>-</td>
<td>0.0125</td>
<td>Coverage factor k = 1 (67%)</td>
</tr>
<tr>
<td>Expanded uncertainty</td>
<td>-</td>
<td>Normal</td>
<td>-</td>
<td>0.0250</td>
<td>Coverage factor k = 2 (95%)</td>
</tr>
</tbody>
</table>

a Standard uncertainty and expanded uncertainty correspond to normally distributed uncertainty with 67% (sometimes denoted one-sigma, or coverage factor k = 1) and 95% coverage probability (k = 2) respectively. Rectangular distributions correspond to the case where errors are equally likely across a range, such as resolution of the balance; the half-width of the distribution is divided by √3 as per the GUM guidance. Conversely, normal distributions generally correspond to cases where the errors are statistical in nature.

b Repeated weighings in situ

c Re-weighing the same thing

d Maximum ambient temperature variation of ±1°C assumed
an uncertainty \( (k = 2) \) of ±0.0027 mg cm\(^{-2}\) for the platinum wire and ±0.0023 mg cm\(^{-2}\) for the Pt-6%Rh and Pt-30%Rh wires.

It was found that all the wires progressively lost mass during high temperature exposure. **Figure 1** shows the mass loss per unit surface area as a function of time of exposure to high temperature. It can be seen that the mass loss is a linear function of elapsed time, at least up to about 150 h. Beyond that, however, a marked departure from linearity is seen, which suggests an acceleration of the mass loss per unit surface area. Intriguingly, previously

![Fig. 1. Mass loss as a function of elapsed time at 1324°C for the three wires studied. Dashed line shows linear guide to the eye for data up to about 150 h; beyond that, there is a marked departure from linearity, where the mass loss appears to accelerate. The error bars (which are approximately the same size as the data points) correspond to the expanded uncertainty from Table I, converted to mass loss per unit area](image1)

![Fig. 2. Very high precision measurements of thermoelectric drift (in temperature terms) as a function of elapsed time at 1324°C for a variety of different thermocouples, after (14). Here the thermocouples are denoted by rhodium content. For instance, '6/0' corresponds to Pt-6%Rh versus platinum. It can be seen that the drift is non-linear up to about 150 h, beyond which there is a 'cross-over' to a linear regime (shown by the dashed 'guides to the eye')](image2)
reported very high precision drift tests of a set of different platinum-rhodium thermocouples (shown in Figure 2) show that they all exhibit a marked change in drift rate at about 150 h as well; beyond about 150 h the drift rate is constant for many hundreds of hours (15). The Pt-30%Rh appears to lose mass fastest, which is what might be expected since this wire contains more rhodium, and the vapour pressure of RhO₂ is higher than that of PtO₂ at this temperature (16).

The fact that the mass change up to about 150 h is linear for the reported measurements is in qualitative agreement with previous results (5, 10, 11). However, the rate of mass loss of platinum, using the data of Jehn (5) and Phillips (10), was 0.0049 mg cm⁻² h⁻¹ and 0.0048 mg cm⁻² h⁻¹ respectively at 1350°C. In the current study, the rate of mass loss up to 150 h was about 0.0006 mg cm⁻² h⁻¹, which is about an order of magnitude lower. This may be because in the present study the wire is enclosed in quite tight-fitting bores to emulate their use in thermocouples, so the reduced rate of mass loss may be due to the establishment of saturated vapour pressure above the wire (inhibiting further evaporation), or reduced oxygen present as the surface oxidation proceeds, or deposition of the oxide vapour or all of these effects. This is in contrast to the previous studies cited, where the samples were bulk (for example, crucibles, meshes, coupons) and the surface was exposed to the surroundings rather than enclosed in tight-fitting bores.

Discussion
The mass losses of platinum, Pt-6% Rh and Pt-30%Rh wires, commonly used for thermocouples, were considered as a function of elapsed time at 1324°C. The wires were placed in thin alumina tubes to emulate the thermocouple format. It was found that the mass loss of the three wires increases linearly with elapsed time, consistent with other investigations, up to an elapsed time of about 150 h, but after that, a marked acceleration of the mass loss is observed.

In the latter case, it is thought that, because the whole length of the thermocouple which develops an output is exposed to the full range of temperatures from room temperature to the measurement junction temperature, the behaviour in the first 150 h (17) arises from early development of microscopic ordering in the platinum-rhodium alloys (during exposure to temperatures below 600°C). This is followed by a slow coating of the platinum-rhodium leg by rhodium oxide (during exposure to temperatures between 600°C and 950°C) (18–22). This is difficult to apply directly to the mass measurements because the all of the wire was held at 1324°C so the oxidation effects at lower temperatures do not occur, but it is conceivable that comparable ordering and coating behaviour is taking place during the slow increase and decrease of the setpoint temperature of the furnace. It is also possible that the mass loss simply varies non-linearly over the whole duration: the motivation for expressing the data in terms of a discontinuity at about 150 h duration has been guided by the previously observed marked increase in the rate of mass for platinum at 1300°C after about 60 h (12) and 400 h (13); and also by the rapid change in thermocouple drift rate at about 150 h. To draw a definitive conclusion on this point, more detailed measurements would be needed, perhaps with the wire exposed to the entire temperature range from ambient to 1324°C.

Conclusion
The rate of mass loss was approximately an order of magnitude less than that observed in previous studies, and the enclosed nature of the wires in the alumina insulation tubes is thought to be a cause of this. Previous high precision studies have shown that a change in the drift rate after about 150 h at 1324°C is also observed in the thermoelectric drift of a wide range of platinum-rhodium thermocouples, and the current results were compared with those studies. The mass loss was greatest for Pt-30%Rh, followed by Pt-6%Rh, then platinum.

Acknowledgements
This work was performed under the auspices of the UK South East Physics Network (SEPNet) scheme, and as part of a European Metrology Programme for Innovation and Research (EMPIR) project to enhance process efficiency through improved temperature control, ’17IND04 EMPRESS 2’. The EMPIR is jointly funded by the EMPIR participating countries within EURAMET and the European Union.

References
5. H. Jehn, *J. Less Common Met.*, 1984, **100**, 321
18. E. S. Webster, *Int. J. Thermophys.*, 2015, **36**, (8), 1909

The Authors

Sivahami Uthayakumaar is currently a third-year PhD student at the University of York, UK, in the Nuclear Physics research group. She is specialising in nuclear structure with emphasis on isospin symmetry and the reasons that lead to this symmetry being broken. This research is studied in the proton-rich region of the chart of nuclides by analysing mirror nuclei (i.e. nuclei that have the proton and neutron numbers interchanged). The work reported in this paper was performed during a placement at the National Physical Laboratory (NPL), UK. She is a Member of the Institute of Physics.

Stuart Davidson is the Science Area Leader for Mechanical Metrology at the UK’s standards laboratory, the NPL. He has been responsible for some major advances in the field of mass measurement including the direct measurement of the density of air, weighing in vacuum and the use of surface analysis to predict the stability of mass standards. He is a past chair of the EURAMET Technical Committee for Mass and Related Quantities and current convenor of the Mass sub-committee and Strategy Working Group. He is also chair of the Consultative Committee for Mass and Related Quantities (CCM) Mass Working Group and the Task Group implementing the ‘new’ kilogram.

Jonathan Pearce is a principal research scientist and head of contact thermometry in the Temperature & Humidity group at the UK’s NPL, where he has been based for 15 years. He has authored 143 technical papers on applied physics and temperature metrology. He specialises in development of temperature standards for the realisation and dissemination of the SI unit of temperature, the kelvin, as well as provision of process monitoring and control solutions for industry, government and academia. He is the UK representative on the EURAMET Technical Committee for Thermometry (TC-T). He is a Fellow of the Institute of Physics.
The principal possibility of processing the industrial poor collective concentrates of platinum group metals (pgms) using a hydrocarbonyl technology with the selective concentration of pgms from poor multicomponent chloride and chloride-sulfate solutions with the subsequent production of pure pgms is shown.

1. Introduction

The pgms can be produced both from natural raw materials and treated pgm materials, including scrap metal and waste in the form of used platinum alloy products, electronic waste or coating materials. They may also be extracted from production induced sources, such as the byproducts of copper–nickel sulfide ore treatment. In all cases of pgm raw material treatment, production involves extracting pure pgms from multicomponent systems in which their content can vary considerably.

Extraction of pgms from natural and synthetic materials uses various technological processes, which include precipitation, extraction, sorption and electrochemical processes in various forms (1).

This study investigates fundamental technological possibilities of concentrating and separating pgms based on hydrocarbonyl processes that occur during the treatment of solutions of pgm chlorocomplexes with carbon monoxide under atmospheric pressure (Figure 1).

Carbon monoxide molecules have a high thermodynamic potential of a reducing agent. For example, for Reaction (i):

\[ 2\text{CO} + \text{O}_2 \rightleftharpoons 2\text{CO}_2 \]  

the \( \Delta G^\circ \) value amounts to \(-314.7\) kJ. However, Reaction (i) does not occur spontaneously, due to high-energy chemical bonds between carbon and oxygen atoms. Nevertheless, in the presence of catalysts, carbon monoxide molecules are activated due to a change in the energy of bonding electrons, and the mixture of carbon monoxide with ambient oxygen gains chemical reactivity as per Reaction (i). For instance, when treating \( \text{H}_2\text{PdCl}_4 \) solution with carbon monoxide, the first stage is the insertion of a carbon monoxide molecule into the inner sphere of the \( \text{PdCl}_4^{2-} \) complex, thereby generating carbonyl chloride complex as per Reaction (ii):

\[ \text{PdCl}_4^{2-} + \text{CO} \rightleftharpoons \text{PdCOCl}_3^- + \text{Cl}^- \]  

As the result of Reaction (ii), free molecules become ligands, which lead to their activation and provoke inner sphere redox process (Reactions (iii)-(iv)):

\[ \text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \]  

\[ \text{Pd}^{2+} + 2\text{e}^- \rightleftharpoons \text{Pd}^0 \]  

This is described by Reaction (v):

\[ \text{PdCOCl}_3^- + \text{H}_2\text{O} \rightleftharpoons \text{Pd}^0 + \text{CO}_2 + 2\text{HCl} + \text{Cl}^- \]  

Reactions (ii) and (v) lead to palladium reduction by carbon monoxide, Reaction (vi):

\[ \text{PdCl}_4^{2-} + \text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{Pd}^0 + \text{CO}_2 + 2\text{HCl} + 2\text{Cl}^- \]
Reaction (vi) reflects the processes occurring in chloride pgm solutions during their treatment with a gas mixture containing carbon monoxide and depicts the nature of the ‘hydrocarbonyl process’ term (2).

The reduction of noble metals by treating their chlorocomplexes with carbon monoxide can be represented by Reactions (vi)–(xiii):

- \[ \text{PtCl}_6^{2-} + 4\text{CO} + 2\text{H}_2\text{O} \rightleftharpoons \text{Pt(CO)}_2^2 + 2\text{CO}_2 + 4\text{HCl} + 2\text{Cl}^- \] (vii)
- \[ \text{RhCl}_6^{3-} + 3\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{Rh(CO)}_2\text{Cl}_2^- + \text{CO}_2 + 2\text{HCl} + 2\text{Cl}^- \] (viii)
- \[ 2\text{Rh(CO)}_2\text{Cl}_2^- + \text{H}_2\text{O} \rightleftharpoons 2\text{Rh}^0 + \text{CO}_2 + 3\text{CO} + 2\text{HCl} + 2\text{Cl}^- \] (ix)
- \[ \text{RuCl}_6^{2-} + 3\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{Ru(CO)}_2\text{Cl}_4^{-2} + \text{CO}_2 + 2\text{HCl} \] (x)
- \[ 2\text{IrCl}_6^{2-} + 7\text{CO} + 3\text{H}_2\text{O} \rightleftharpoons 2\text{Ir}^0 + \text{CO}_2 + 3\text{CO}_2 + 6\text{HCl} + 2\text{Cl}^- \] (xi)
- \[ 2\text{AuCl}_6^{3-} + 3\text{CO} + 3\text{H}_2\text{O} \rightleftharpoons 2\text{Au}^0 + 3\text{CO}_2 + 6\text{HCl} + 6\text{Cl}^- \] (xii)
- \[ 2\text{AgCl}_2^- + \text{CO} + \text{H}_2\text{O} \rightleftharpoons 2\text{Ag}^0 + \text{CO}_2 + 2\text{HCl} + 2\text{Cl}^- \] (xiii)

All these reactions are preceded by reactions in which chloride complexes are converted into various carbonyl chloride complexes. The latter can be further subjected to inner sphere redox processes generating either metals (Reactions (vii), (ix), (xii), (xiii)) or carbonyl chloride complexes in which metals have low oxidation states (Reactions (vii), (viii), (x), (xi)).

The capacity of noble metals to enter a free state is defined by the following series: gold > palladium > platinum > rhodium (2).

This study explores the opportunities of applying hydrocarbonyl processes in the separation and concentration of pgms from multicomponent systems represented by the industrial lean bulk concentrates of pgms (copper and nickel anode sludges) and rich bulk concentrates of pgms (concentrates predominantly containing: (a) platinum and gold; (b) rhodium, ruthenium and silver; or (c) iridium).

The principles of hydrocarbonyl technology for the treatment of various pgm industrial concentrates as stated in (3), where copper–nickel anode sludges with the high contents of copper, nickel, iron, selenium and tellurium were used as primary products, have become a foundation for further feasibility studies of reprocessing lean and rich bulk pgm concentrates using hydrocarbonylation.

2. Experimental Section

Laboratory experiments on hydrocarbonyl processes were conducted using pgm chlorocomplex solutions generated from corresponding chloride reactants (standardised test solutions), chloride and chloride–sulfate solutions generated through the

![Schematic of one of the options of the hydrocarbonyl processes of concentration and separation of precious metals](https://doi.org/10.1595/205651321X16086477340586)
hydrochlorination of industrial products, such as anode sludges generated during the extraction of cathode copper and nickel, and pgm concentrates used in refining.

Carbon monoxide was obtained by treating hot sulfuric acid with formic acid. After collecting, carbon monoxide was stored in gasometers. The reactions took place in glass reactors equipped with mechanical stirrers. Moreover, analytical support was provided through atomic absorption and chemical analyses.

2.1 Treatment of Lean Bulk pgm Concentrates

For this experiment, chloride and the chloride–sulfate solutions of industrial copper and nickel anode sludges were used. Their contents are listed in Tables I and II.

2.1.1 Treatment of Copper Anode Sludge Solution

Carbon monoxide was bubbled through 500 ml of a solution (see Table I) while stirring vigorously at 97–98°C and atmospheric pressure for 7 h. A black-coloured precipitate was obtained. The suspension was cooled down in carbon monoxide atmosphere and vacuum filtered. Thereafter, the obtained residue was washed with 2 M HCl. The obtained black precipitate was calcined at 900°C until a metal sponge was formed (C-1). This was accompanied by the distinctive odour of SeO₂ and TeO₂. The obtained C-1 was dissolved in aqua regia and analysed for the content of noble and non-ferrous metals. Upon the analysis of the obtained solution, the content of C-1 was found to be as presented in Table III.

After the isolation of C-1, the filtrate was extracted with isoamyl alcohol at room temperature while stirring for 15 min in five stages with an aqueous-to-organic phase ratio of 5:1. Both extraction phases as well as wash waters from C-1 were analysed for the contents of noble metals. Their breakdown by conversion products is shown in Table IV. Table IV indicates that the consecutive processes of hydrocarbonylation and liquid extraction result in reasonably full extraction of noble metals from the copper anode sludge solution into two products: sufficiently selective C-1 and organic phase (isoamylic extract).

To define the parameters of the hydrocarbonylation process where the coprecipitation of rhodium with palladium and platinum in C-1 is eliminated, a series of experiments on the hydrocarbonylation of standardised test solutions containing chlorocomplexes platinum(IV), palladium(II), rhodium(III), ruthenium(IV) and iridium(IV) were conducted at various temperatures and hydrochloric acid concentrations. Obtained precipitates and filtrates were analysed for pgm content, which allowed the rate of pgm extraction

### Table I Composition of Copper Anode Sludge Solution

<table>
<thead>
<tr>
<th>Component</th>
<th>Content, g l⁻¹</th>
<th>Component</th>
<th>Content, g l⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>~50.000</td>
<td>Pt</td>
<td>2.0000</td>
</tr>
<tr>
<td>Ni</td>
<td>~30.000</td>
<td>Au</td>
<td>0.2390</td>
</tr>
<tr>
<td>Fe</td>
<td>~3.000</td>
<td>Ag</td>
<td>0.3910</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>214.000</td>
<td>Rh</td>
<td>0.2080</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>67.500</td>
<td>Ru</td>
<td>0.0630</td>
</tr>
<tr>
<td>Pd</td>
<td>5.763</td>
<td>Ir</td>
<td>0.0104</td>
</tr>
</tbody>
</table>

### Table II Composition of Nickel Anode Sludge Solution

<table>
<thead>
<tr>
<th>Component</th>
<th>Content, g l⁻¹</th>
<th>Component</th>
<th>Content, mg l⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>15.500</td>
<td>Rh</td>
<td>41.4</td>
</tr>
<tr>
<td>Ni</td>
<td>10.500</td>
<td>Ru</td>
<td>8.7</td>
</tr>
<tr>
<td>Fe</td>
<td>3.000</td>
<td>Ir</td>
<td>3.6</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>179.500</td>
<td>Ag</td>
<td>86.7</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>19.400</td>
<td>Au</td>
<td>0.2</td>
</tr>
<tr>
<td>Pd</td>
<td>1.304</td>
<td>Se</td>
<td>171.0</td>
</tr>
<tr>
<td>Pt</td>
<td>0.323</td>
<td>Te</td>
<td>102.0</td>
</tr>
</tbody>
</table>
to be defined for each product. Results are given in Table V. The analysis of these results shows that the coprecipitation of rhodium with platinum and palladium during the hydrocarbonylation of chlorocomplex solutions platinum(IV), palladium(II) and rhodium(III) does not occur at HCl concentrations ≥ 2 mol l\(^{-1}\) and temperatures ≤ 80°С. These conditions were taken into account during the study of the treatment process of the nickel electrolyte sludge solution.

### 2.1.2 Treatment of Nickel Anode Sludge Solution

In a series of experiments, 0.5 l to 0.7 l of nickel anode sludge solution (see Table II) was treated with carbon monoxide under atmospheric pressure, temperature of 20–60°С and HCl concentration of 2.0 mol l\(^{-1}\) while stirring vigorously. Obtained black-coloured finely dispersed precipitates were separated by filtration under

<table>
<thead>
<tr>
<th>Component</th>
<th>Content, wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd</td>
<td>64.41</td>
</tr>
<tr>
<td>Pt</td>
<td>24.58</td>
</tr>
<tr>
<td>Au</td>
<td>2.76</td>
</tr>
<tr>
<td>Ag</td>
<td>4.42</td>
</tr>
<tr>
<td>Rh(^a)</td>
<td>2.48</td>
</tr>
<tr>
<td>Ir</td>
<td>not detected</td>
</tr>
</tbody>
</table>

\(^a\)Rh coprecipitates as a result of the high temperature of hydrocarbonylation

<table>
<thead>
<tr>
<th>Table IV Breakdown of Noble Metals by Products Obtained from Copper Anode Sludge Solution Using Carbonyl Extraction Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal</td>
</tr>
<tr>
<td>---------------------</td>
</tr>
<tr>
<td>Pd</td>
</tr>
<tr>
<td>Pt</td>
</tr>
<tr>
<td>Rh</td>
</tr>
<tr>
<td>Ru</td>
</tr>
<tr>
<td>Ir</td>
</tr>
<tr>
<td>Au</td>
</tr>
<tr>
<td>Ag</td>
</tr>
</tbody>
</table>

\(^a\)Se and Te are precipitated into C-1 almost completely and can be removed by calcination
\(^b\)Rh precipitated into C-1 as a result of high hydrocarbonylation temperature

<table>
<thead>
<tr>
<th>Table V Precipitation of pgm When Using Carbon Monoxide Under Atmospheric Pressure on Standardised Test Solutions Containing Chlorocomplexes Platinum(IV), Palladium(II), Rhodium(III), Ruthenium(IV), Iridium(IV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. of standardised test solution(^a)</td>
</tr>
<tr>
<td>---------------------------------------------</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>3</td>
</tr>
<tr>
<td>4</td>
</tr>
<tr>
<td>5</td>
</tr>
</tbody>
</table>

\(^a\)Hydrocarbonylation conditions:
No. 1. t = 100°С; for 2.5 h; bubbling, no stirring
No. 2. t = 100°С; for 3.0 h; bubbling, no stirring
No. 3. t = 80°С; for 3.0 h; bubbling, with stirring
No. 4. t = 50°С; for 3.0 h; bubbling, with stirring
No. 5. t = 50°С; for 3.0 h; bubbling, with stirring
vacuum and washed with 2 M HCl. These precipitates were analysed without calcination. Table VI lists the results of the analysis, which shows that reasonably a full separation of pgms into two selective products occurred: black fine precipitate containing platinum, palladium, gold, silver, selenium and tellurium; and solution containing rhodium, ruthenium, iridium and non-ferrous metals.

2.2 Treatment of Industrial pgm Rich Bulk Concentrates

Section 2.1 demonstrated the capability of extracting and concentrating pgms from the solutions of their lean bulk concentrates, for example copper and nickel anode sludges. At the same time, the capability of using hydrocarbonylation to treat the rich bulk concentrates of pgms is also of great technological interest. These concentrates are represented by, in particular, three types (pgm concentrates predominantly containing: (a) platinum and palladium, M-1; (b) rhodium, ruthenium and silver, M-2; (c) iridium, M-3; and (d) speiss alloy). At present, the refinement of such concentrates is conducted under separate processes (1).

To conduct an experimental treatment through hydrocarbonylation, a total chloride solution obtained by the hydrochlorination of concentrates M-1, M-2 and M-3 at the ratio of 4:2:1 was used. During the hydrochlorination process of the concentrate mixture, silver was removed as AgCl precipitate. Thereafter, from the obtained solution, gold was extracted by treating it with Fe$_2$(SO$_4$)$_3$ solution. Table VII describes the content of the obtained solution. Within the experiment, carbon monoxide was bubbled through 20 ml of the original solution (see Table VII) under atmospheric pressure and temperature of 70°C while stirring vigorously for 3.33 h.

<table>
<thead>
<tr>
<th>Table VI Composition of the Black Precipitate Obtained by the Hydrocarbonylation of Nickel Anode Sludge Solution (see Table II) $^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Content, wt%</strong></td>
</tr>
<tr>
<td>Pt</td>
</tr>
<tr>
<td>Pd</td>
</tr>
<tr>
<td>Au</td>
</tr>
<tr>
<td>Ag</td>
</tr>
<tr>
<td>Rh</td>
</tr>
<tr>
<td>Σ Pt, Pd, Au, Ag, Rh</td>
</tr>
<tr>
<td>Se</td>
</tr>
<tr>
<td>Te</td>
</tr>
<tr>
<td>Σ Se, Te</td>
</tr>
<tr>
<td>Ni</td>
</tr>
<tr>
<td>Fe</td>
</tr>
<tr>
<td>Cu</td>
</tr>
<tr>
<td>Σ Ni, Fe, Cu</td>
</tr>
<tr>
<td>Σ $^b$ total</td>
</tr>
</tbody>
</table>

$^a$ Treatment conditions: PCO = atmospheric pressure; t = 20–60°C; treatment time 3–4 h
$^b$ All precipitate contains approximately 1.50 wt% of SiO$_2$
The solution was observed to acquire black colour as a result of the generation of finely dispersed powders of palladium and platinum, which were easily filtered out with a vacuum filter. The filtrate was red and brown. The obtained precipitate was washed with 2 M HCl, dried and weighed. 0.5515 g of black-coloured powder was generated. The precipitate possessed large specific surface area and high absorbing capacity, thereby required thorough washing.

The analysis of the powder and filtrate for the content of palladium, platinum, gold, rhodium, ruthenium and iridium showed almost full precipitation of palladium, platinum and gold (none of the elements were found in the filtrate), no ruthenium and iridium were found in the powder, and the extraction rate of rhodium from the solution amounted to approximately 1%.

It is worth noting that platinum from the solution is not recovered as metal, but as its oligomeric dicarbonyl \([\text{Pt(CO)}_2]_n\), where \(n\) is divisible by three. Palladium is extracted in its native form, together with its amorphous carbon phase (4).

In another experiment, 50 ml of the original solution (see Table VII) was treated with carbon monoxide under atmospheric pressure and temperature of 95°C for 4.5 h while stirring vigorously. Finely dispersed black powder was produced. After filtering, washing with 2 M HCl and air drying, 1.3501 g of a black powder were recovered, which was analysed for the content of noble metals (Table VIII).

The filtrate, which was yellow and green, was extracted twice with 10 ml of isoamyl alcohol. The organic phase coloured in yellowish was boiled dry without calcination. The boiled organic phase was analysed for the content of noble metals (Table VIII).

The results of the laboratory treatment of the mixture of concentrates M-1, M-2 and M-3 show that the hydrocarbonylation process can be successfully used at the primary stage of refinement, and this allows to separate rhodium, ruthenium and iridium from other noble metals and makes the subsequent extraction of platinum and palladium, as well as rhodium, ruthenium and iridium easier.

To confirm the possibility of extracting rhodium, ruthenium and iridium using the traditional technology of the nitration of their carbonyl chloride solutions, which are left after extracting the concentrate of platinum, palladium, gold, tellurium and selenium by hydrocarbonylation, a process solution of speiss with the following content (g l\(^{-1}\)) was used: platinum, 20.02; palladium, 53.00; rhodium, 6.50; ruthenium, 0.50; iridium, 2.70; gold, 0.82; tellurium, 3.00; selenium, 2.30; copper, 16.40; lead, 3.70; bismuth, 3.85; nickel, 2.90; iron, 1.55; HCl, 100.00. Carbon monoxide was bubbled through 500 ml of the specified solution at 60°C under atmospheric pressure for 4 h while stirring vigorously. This generated the precipitate of \(\Sigma\) platinum, palladium, gold, selenium, tellurium, which was washed with 2 M HCl after the separation. The precipitate and filtrate were analysed for the content of original components. It was concluded that gold, palladium, selenium and tellurium precipitated fully whereas platinum precipitated by 98%. The solution after the precipitation of \(\Sigma\) platinum, palladium, gold, selenium, tellurium was nitrated with the precipitation of rhodium in

<table>
<thead>
<tr>
<th>Table VII Composition of the Solution Obtained by the Hydrochlorination of M-1, M-2 and M-3 Concentrate Mixture after Silver and Gold Extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Content, mg l(^{-1})</strong> &amp; Pd &amp; Pt &amp; Rh &amp; Ru &amp; Ir &amp; Au &amp; HCl</td>
</tr>
<tr>
<td>18200 &amp; 5440 &amp; 615 &amp; 160 &amp; 200 &amp; 1.65 &amp; 85500</td>
</tr>
</tbody>
</table>

\(a\) Se and Te contents were not defined

<table>
<thead>
<tr>
<th>Table VIII Breakdown of pgm Byproducts Obtained with M-1, M-2 and M-3 Concentrate Mixture Chloride Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Product</strong></td>
</tr>
<tr>
<td>&amp; Pt &amp; Pd &amp; Au &amp; Rh (^a) &amp; Ru (^b) &amp; Ir (^b)</td>
</tr>
<tr>
<td>Black powder (precipitate after hydrocarbonylation)</td>
</tr>
<tr>
<td>Organic phase of extraction</td>
</tr>
</tbody>
</table>

\(a\) Rh coprecipitates due to the high temperature of hydrocarbonylation. Its presence can also be explained by the inadequate washing of the precipitate

\(b\) Not the full transition of Ru and Ir to the organic phase of extraction is consistent with their breakdown ratio (2)
the form of its ammonium-sodium hexanitrate: \((\text{NH}_4)_2\text{NaRh(NO}_2)_6\).

Thus, the compatibility of hydrocarbonylation and the subsequent processes of the traditional saline extraction technology for rhodium, ruthenium, iridium (1) has been shown.

### 2.3 Sorptive Extraction of Rhodium, Ruthenium and Iridium

Technologies for the extraction of pgms from their chlorocomplexes utilise sorption on ion exchange resins (1). Thus, exploring the opportunity of using sorption for the solutions of carbon chloride anionic complexes \(\text{Rh(I)}–\text{Rh(CO)}_2\text{Cl}^-\), \(\text{Ru(II)}–\text{Ru(CO)}_2\text{Cl}_4^{2-}\) and \(\text{Ir(I)}–\text{Ir(CO)}_2\text{Cl}^-\) to extract rhodium, ruthenium, iridium was appropriate.

To this extent, we used a solution of chlorocomplexes \(\text{RhCl}_6^{3-}\), \(\text{RuCl}_6^{2-}\) and \(\text{IrCl}_6^{2-}\) containing (mg l\(^{-1}\)): rhodium, 260.3; ruthenium, 83.0; iridium, 63.8 and HCl, 2 mol l\(^{-1}\), and a solution of carbonyl chloride anionic complexes rhodium(I), ruthenium(II) and iridium(I), obtained by treating a similar solution of chlorocomplexes \(\text{RhCl}_6^{3-}\), \(\text{RuCl}_6^{2-}\) and \(\text{IrCl}_6^{2-}\) with carbon monoxide at 80°C for 2 h, which led the solution to change its colour from red and brown to yellowish, which is a distinct feature of carbonyl chloride anions rhodium(I), ruthenium(II) and iridium(I).

Both solutions were engaged with gel anion exchange resin based on the copolymer of styrene and divinylbenzene with benzene-pyridinium functional groups (ammonium molybdophosphate (AMP)) while stirring for 2 h. The solutions were then analysed for the content of rhodium, ruthenium and iridium. Results for the observed sorption rate are given in **Table IX**. The results given in **Table IX** show that the processes of hydrocarbonylation and sorption are sufficiently technologically compatible.

### 2.4 Selective Extraction of Rhodium, Ruthenium and Iridium

Given the specific properties of carbonyl chloride complexes rhodium(I), ruthenium(II), iridium(III) (2), it was of interest to obtain the experimental results of their reaction with hydrogen under atmospheric pressure, as it is known that chlorocomplex solutions rhodium(III), ruthenium(IV), iridium(IV) only react with hydrogen at high pressure (5). For this experiment, a standardised test solution of chlorocomplexes rhodium(III), ruthenium(IV), iridium(IV) in 2 M HCl with the following metal concentration (mg l\(^{-1}\)): 168.0; 119.0; 70.0, respectively, was treated with carbon monoxide under atmospheric pressure and temperature of 95°C for 2 h. The solution was observed to quickly lose its original red and brown colour and turned a yellowish colour, which is a characteristic of carbonyl chloride complexes rhodium(I), ruthenium(II), iridium(I). Thereafter, at the same conditions, hydrogen was fed to the reactor instead of carbon monoxide. This provoked the solution to gain black colouration and precipitate. The hydrogen treatment lasted 6 h. The obtained precipitate was filtered out and dissolved in the mixture of HCl and \(\text{H}_2\text{O}_2\). The atomic absorption analysis of the precipitate and filtrate has shown that the resulting black precipitate comprised rhodium without ruthenium and iridium content, and that the filtrate contained almost no rhodium. The filtrate was neutralised to pH 5 and treated with hydrogen under the same conditions. The solution gained black colour and released a black precipitate. The hydrogen treatment lasted 6 h. The black precipitate was filtered out and dissolved in the mixture of HCl and \(\text{H}_2\text{O}_2\). The atomic absorption analysis of this solution showed that it contained ruthenium only, whereas the analysis of the solution after filtering out black ruthenium showed that there was almost no ruthenium in it. The yellowish filtrate was treated with chlorine gas, which produced intense red colouration characteristic for chlorocomplex iridium(IV). \(\text{NH}_4\text{Cl}\) in the form of saturated aqueous solution was added to this solution. This resulted in the black precipitation, characteristic for \((\text{NH}_4)_2\text{IrCl}_6\). The above-precipitate solution analysis showed trace amounts of iridium.

The described experiment has shaped a foundation for conducting a series of experiments aimed to

---

**Table IX Results of Sorption of Chlorocomplexes Rhodium(III), Ruthenium(IV), Iridium(IV) and Carbonyl Chloride Complexes Rhodium(I), Ruthenium(II) and Iridium(I) by Anionic AMP Resin**

<table>
<thead>
<tr>
<th>Solution type</th>
<th>pgm sorption rate on anionic AMP resin, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rh</td>
</tr>
<tr>
<td>Chlorocomplexes</td>
<td>85.9</td>
</tr>
<tr>
<td>Carbonyl chloride complex</td>
<td>80.3</td>
</tr>
</tbody>
</table>

*Room temperature for 2 h and resin-solution ratio of 1:50*
optimise pgm reduction processes, which allowed to formulate the method for selective extraction of rhodium, ruthenium and iridium from rhodium(I), ruthenium(II) and iridium(I) carbonyl chloride solutions by treating them with hydrogen under atmospheric pressure (6).

2.5 Impact of Carbon Monoxide Content in the Gas Mixture on pgm Reduction Rate

Reactions (vi)–(xiii) have some induction period ($\tau_{\text{ind.}}$), i.e. time from the beginning of the treatment of the pgm chloride solution with carbon monoxide until black pgm precipitation or change in original colour. The induction period of the hydrocarbonylation is impacted by temperature, stirring speed, partial pressure of carbon monoxide and $\text{H}^+$ and $\text{Cl}^-$ ion concentration (2).

Studies were conducted to identify the impact of the carbon monoxide content in the reaction gas ($\text{P}_{\text{CO}}$) on the induction period of a hydrocarbonyl process. As an example, we provide the results of the studies on the impact of $\text{P}_{\text{CO}}$ on the induction period of Reaction (vi) (Table X). The original $\text{H}_2\text{PdCl}_4$ solution contents were as follows: $\text{[Pd(II)]}$, 167 mg l$^{-1}$; $\text{HCl}$, 2 mol l$^{-1}$; solution volume, 75 ml; $\text{CO + N}_2$ mixture bubbling rate, 100 ml min$^{-1}$; stirring speed, 1000 rpm; temperature, 50°C. The length of the induction period of Reaction (vi) was calculated based on the automatic logging of changes in the light transmission value of the solution.

The experimental data provided in Table X indicate that air-producer gas can be used for conducting hydrocarbonyl processes in technological operations, as the significant decrease in the hydrocarbonylation rate is observed when carbon monoxide content in the $\text{CO + N}_2$ mixture does not exceed 20% whereas air-producer gas contains 25% of carbon monoxide.

3. Discussion of Results

The provided results of laboratory studies for the processes of the generation and breakdown of carbonyl pgm complexes, which take place when the solutions of their chlorocomplexes are treated with carbon monoxide under atmospheric pressure and cause pgm chlorocomplexes to turn into carbonyl chloride complexes with low oxidation state metals or to the full reduction of pgms, allow use of these processes to conduct selective pgm concentration from multicomponent solutions with the subsequent individual extraction of metals. This can become innovative in pgm hydrometallurgy.

A significant technological advantage of the hydrocarbonyl technology is the ability to separate original chloride and chloride–sulfate multicomponent solutions containing pgm in a wide concentration range (from tens of grams per litre to some milligrams per litre) and heavy non-ferrous metals in large amounts into two products. Platinum and palladium, along with gold, silver, selenium and tellurium, precipitate quite effectively, when rare pgms (rhodium, ruthenium and iridium) along with non-ferrous metals remain in the solution, transiting from their chlorocomplexes to carbonyl chloride anionic complexes where metals have low oxidation states: rhodium(I), ruthenium(II), iridium(I) with their specific properties, which makes the subsequent separation process easier.

Another advantage of the hydrocarbonylation process is that the separation of original multicomponent chloride solutions containing pgm into two products can be conducted in one step at the very beginning of the manufacturing process using only one reactant, i.e. cheap and available air-producer gas containing approximately 25% of carbon monoxide and 75% nitrogen in volume.

Moreover, several factors affect the results of the hydrocarbonyl processes; therefore, control possibilities for these processes can be extended to ensure that they occur as desired. This significantly distinguishes the hydrocarbonyl technology from all other technologies used in this field. Thus, it was demonstrated (2) for the Reaction (vi) that the palladium reduction rate has the following functional

<table>
<thead>
<tr>
<th>CO content in CO + N$_2$ mixture, vol%</th>
<th>100</th>
<th>70</th>
<th>50</th>
<th>33</th>
<th>16</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction (vi) induction period, $\tau_{\text{ind.}}$, s</td>
<td>58</td>
<td>62</td>
<td>65</td>
<td>67.5</td>
<td>70.5</td>
<td>135</td>
</tr>
</tbody>
</table>
dependence on the component concentration, Equation (xiv):

\[
\frac{d[Pd(0)]}{dT} = f([Pd(II)], [H_2O]^2, [H^+]^{-2}, [Cl^-]^{-1}, P_{CO}^n}
\]  
(xiv)

where \( n = 0.5 \) at \( P_{CO} \geq 30 \text{ kPa}; n = 1.0 \) at \( P_{CO} \leq 30 \text{ kPa} \).

By changing the contents of the original solution along with the carbon monoxide content in the reaction gas and temperature, one can significantly influence the rate of hydrocarbonyl processes and their final result. Thus, when treating the palladium dichloride solution with carbon monoxide in 10 M HCl at 50°C, Reaction (vi) does not go to completion, and its colour changes from red and brown (original solution) to yellow and green. When caesium chloride crystals are introduced to the solution, small yellow and green crystals comprising Cs[PdCOCl₃] are generated (2).

4. Conclusion

The results of this study demonstrate the technological potential of hydrocarbonyl processes for the selective concentration of pgms from multicomponent chloride–sulfate solutions with the subsequent production of pure metals. Furthermore, hydrocarbonyl processes can be combined with existing technologies, such as precipitation in the form of complex salts, extraction and sorption, which expands their technological application. This is supported by the results of our latest studies (6–9). Hydrocarbonyl processes are also of interest in the chemistry of pgms (4).

References

2. I. V. Fedoseev, “Hydrocarbonyl Processes in the Technology of the Platinum Metals”, Ore and Metals Publishing House, Moscow, Russia, 2011, 128 pp
5. V. G. Tronev, Bull. Acad. Sci. URSS, Série chim., 1937, 2, 334
6. I. V. Fedoseev, V. V. Vasekin, M. V. Maramygina and N. V. Rovinskaya, ‘Method for the Selective Extraction of Rhodium RH, Ruthenium RU and Iridium IR from Hydrochloric Acid Solutions of Chlorine Complexes of Platinum PT (IV), Palladium PD (II), Gold AU (III), Silver AG (I), Rhodium RH (III), Ruthenium RU (IV) and Iridium IR (IV)’, Russian Patent Appl. 2020/119,883
8. I. V. Fedoseev, V. V. Vasekin, and N. V. Rovinskaya, Johnson Matthey Technol. Rev., 2020, 64, (1), 42

The Authors

Professor Igor V. I. Fedoseev is Doctor of Technical Sciences and a graduate of the Chemical Faculty of the Lomonosov Moscow State University, Russia. He previously worked at Norilsk Nickel, Russia. He was engaged in the study of carbonyl chloride complexes of platinum metals and defended his thesis and doctoral dissertation in chemistry and technology of carbonyl chloride complexes of pgms. His area of scientific interest is the chemistry of carbonyl complexes of pgms and their technological use. He is the author of two monographs.
Yuriy A. I. Kotlyar, PhD (Technical Sciences), graduated from the Moscow Machine Tool Institute, Russia, with a degree in machines and foundry technology. He worked as General Director of RAO Norilsk Nickel, General Director of JSC Gipronickel Institute, Chairman of the Board of Directors of RAO Norilsk Nickel, Chairman of the Bureau of the Coordination Council of the Union of Scientific-Technical Society of Scientists, specialists in the production and processing of non-ferrous metals, gold and diamonds. He is a member of the Supervisory Board of the Golden Club of Russia, a lecturer at the Moscow Institute of Steel and Alloys, a State Prize Laureate and General Consultant of PJSC Norilsk Nickel.

Vasily V. Vasekin, PhD (Chemistry), General Director of Supermetal JSC, is a graduate of the Chemical Faculty of Lomonosov Moscow State University, Russia. He is engaged in metallurgy and chemistry of platinum alloys and materials based on them. He conducts research and develops technologies using composite materials based on platinum alloys in the production of glass-melting devices and catalytic systems.

Natalya V. Rovinskaya, PhD (Chemistry), Senior Researcher, is a graduate of the Lomonosov Moscow Institute of Fine Chemical Technology, Russia. She was engaged in the problems of synthesis of semi-synthetic antibiotics. She defended her thesis on the methods of synthesis of doxycycline. She is currently engaged in technological work on the separation of pgms from industrial wastes and their purification by hydrolytic methods and the development of methods for the analysis of pgms and their alloys.
Renyao Zhang, Junmei Guo, Chuanjun Wang, Limin Zhou, Ming Wen*
State Key Laboratory of Advanced Technologies for Comprehensive Utilization of Platinum Metals, Kunming Institute of Precious Metals, Kunming 650106, China

*Email: wen@ipm.com.cn

Ruthenium tablets with mean grain size of \(~4–5\ \mu m\) were prepared by vacuum hot pressing (VHP), and tablets with maximum density of \(12.2 \text{ g cm}^{-3}\) were obtained with sintering time of 2 h. X-ray diffraction (XRD) revealed that there was a texture change with sintering time. The microstructure of the ruthenium tablets was observed by electron backscatter diffraction (EBSD) and field emission scanning electron microscopy (FSEM). The microstructure evolution of ruthenium with sintering time is discussed.

1. Introduction

The refractory platinum group metal ruthenium exhibits unique properties such as high melting point (2334°C) (1), conductivity (\(1.348 \times 10^7 \Omega \text{ m}\)) (2) and high hardness (\(~337\ \text{ DPN}\) for as-melted ruthenium surface) (3). Ruthenium has been used as an active catalyst in applications such as ammonia synthesis and chemical water splitting (4, 5). Ruthenium-based thin films have gained considerable research interest especially in the electronics industry. They have been widely used as electrode materials for dynamic random access memory (DRAM) (6), perpendicularly magnetised heterostructures (7) and as a seed layer material for copper interconnects or transparent conductive zinc oxide (8–10). These uses can be attributed to the low resistivity of ruthenium, its relatively high work function and its low reactivity with various metals. Magnetron sputtering via a ruthenium sputtering target is a well-known technique for ruthenium film deposition since the deposition process provides excellent productivity and is widely used for mass production (11–14). Ruthenium sputtering targets having a homogeneous fine-grained structure are vital for the preparation of high-quality ruthenium films. The powder metallurgy (PM) technology technique of VHP is used for manufacturing ruthenium sputtering targets. To the best of the present authors’ knowledge, although some work has been done on the residual stress of ruthenium sintered by spark-plasma-sintering (SPS) and VHP (15, 16), there are very few published works on the structural evolution of ruthenium during VHP which is quite important for the industrial application of ruthenium sputtering targets. In the present work, the structure and microhardness of ruthenium tablets prepared by VHP are examined and discussed.

2. Material and Methods

2.1 Sample Preparation

High-purity ruthenium powder (99.995 wt%) with an average particle size of 5 μm provided by the Kunming Institute of Precious Metals, China, was used as the raw material. Ruthenium samples were compacted under a pressure of 40 MPa at 1250°C in a vacuum of \(10^{-3}\ \text{ Pa}\) at a heating rate of 15°C min\(^{-1}\) for 0.5 h, 1 h, 2 h, 3 h and 4 h. After sintering, the power was turned off, the tablets were cooled in the furnace to room temperature before being taken.
out. The prepared samples had the shape of a tablet with a diameter of 30 mm and a height of 4 mm.

### 2.2 Microstructure and Properties Characterisation

The density of the samples was measured by Archimedes’ method (17). The phase content of the samples was examined with the help of the X’Pert PRO X-ray diffractometer (PANalytical, The Netherlands) and the SmartLab 9 Kw (Rigaku Corporation, Japan) operated by copper K\(_\alpha\) irradiation. The morphology of the ruthenium samples and their fracture surfaces were studied on the Sirion 200 field emission scanning electron microscope and the Versa 3D\textsuperscript{TM} DualBeam\textsuperscript{TM} (FEI Company, USA) including EBSD. The fracture surface was prepared as follows: firstly, a ruthenium tablet of \(10 \times 4 \times 0.5\) mm was cut by electric discharge machining (EDM); then the disc was polished by abrasive paper until the thickness was \(\sim 200\) µm; finally, the thin slice was bent by hand. A Leica EM TIC 3X ion beam milling system (Leica Microsystems Gmbh, Germany) was used to prepare the sample’s surface for EBSD analysis. The Vickers microhardness of the samples was measured with the help of the HXS-1000A microhardness tester (Shanghai Highwell Optoelectronics Technology Co, Ltd, China) with a load of 100 g.

### 3. Results and Discussion

#### 3.1 Microstructure Characterisation

The density results are shown in [Figure 1](https://doi.org/10.1595/205651321X16183288904988). It can be seen that the sample density increases with sintering time between \(\sim 0.5–2\) h, then decreases after 4 h. The maximum density of ruthenium was 12.2 g cm\(^{-3}\) with a sintering time of 2 h. The XRD spectra of the ruthenium samples are given in [Figure 2](https://doi.org/10.1595/205651321X16183288904988). Ruthenium powder exhibits random orientation of the particles corresponding to the standard PDF card of ruthenium (PDF #06-0663) (18). The intensities of (10\(\bar{1}\)0) and (10\(\bar{1}\)1) peaks decrease sharply, the intensity of (0002) peak increases, while the intensities of (0002) and (10\(\bar{1}\)1) peaks are the same in the samples sintered for 0.5 h. The samples sintered for 1 h show similar XRD patterns. This indicates that a stable grain structure forms in the ruthenium samples after 1 h. The intensity of (10\(\bar{1}\)1) peak began to increase after sintering for 2 h and 4 h. The intensity of (10\(\bar{1}\)0) peak increased again in the sample sintered for 4 h. A stable (0002) texture was formed in the ruthenium samples sintered for 0.5–2 h; however, it disappeared after 4 h. This finding has shown that the texture is controlled by varying the sintering time.

Ruthenium powder is shown in [Figure 3](https://doi.org/10.1595/205651321X16183288904988). It consists of particles having irregular shapes with sizes from 1 µm to 15 µm ([Figure 3(a)](https://doi.org/10.1595/205651321X16183288904988)). The large particles are aggregates of the small particles. There are many pores or voids in the particles ([Figure 3(b)](https://doi.org/10.1595/205651321X16183288904988)), which were caused by gas released during the chemical reduction of ruthenium. The apparent density and the tap density of ruthenium powder were 1.9 g cm\(^{-3}\) and 3.2 g cm\(^{-3}\), respectively. Morphology of the fracture surfaces of ruthenium samples are given in [Figure 4](https://doi.org/10.1595/205651321X16183288904988). Their fracture mode is attested as brittle intergranular fracture (19). This finding agrees with the conclusion that ruthenium behaves like a brittle solid even at elevated temperatures (20). This is a puzzling behaviour because a hexagonal close-packed (HCP) metal is a ductile material (21). The slip of dislocations on both prismatic and basal planes could happen in ruthenium single crystals at room temperature (22). However, basal slip is the main deformation mode of ruthenium single crystals at room temperature under tension and their fracture mode is brittle transgranular fracture (23). The grains in the samples are homogeneous having a size of \(\sim 4–5\) µm, which does not depend on the sintered time.

In order to further reveal the sintering mechanism, EBSD was used to analyse the microstructure. [Figure 5](https://doi.org/10.1595/205651321X16183288904988) is the grain boundary map of ruthenium. Firstly, it can be seen that the grain size of the ruthenium samples with different sintering time is \(\sim 4–5\) µm, corresponding well with...
the fracture surface (Figure 4). The grain interior shows different morphologies with sintering time. For ruthenium sintered for 0.5 h, there are few twins and low-angle grain boundaries (~5–15°) in the grain interior (Figure 5(a)). For ruthenium sintered for 1 h, Figure 5(b) shows clean grain structure with fewer low-angle grain boundaries as compared with Figure 5(a). Twins and low-angle grain boundaries with high density appear inside grains when sintering time reaches 2 h (Figure 5(c)), and then the defect density decreases again in the sample sintered for 4 h. The statistical results of grain boundaries are summarised in Table I. From Table I, it can be seen that the total length of low-angle grain boundaries is only 1.8 µm for ruthenium sintered for 1 h which is the shortest of all the samples. The total length of low-angle grain boundaries is 42 µm for ruthenium sintered for 2 h, which is the longest of all the samples. The total length of boundaries increases from ~0.5–2 h, achieving a maximum value with sintering time of 2 h (263 µm), and then decreases to 141 µm with sintering time of 4 h. For some HCP metals, the activation of twins shows a strong dependence on the deformation temperature and strain rate. During the hot compression of titanium at temperatures from 673 K to 973 K, Zeng et al. found many twins at 723 K and 0.1 s⁻¹, few twins after deformation at 723 K and 0.01 s⁻¹ and no twins after deformation at 973 K and 0.01 s⁻¹ (24). Ruthenium possesses an HCP lattice, where twinning is the important stress accommodation channel under mechanical loading (21). Experiment has shown that there are four active twin systems: 94.8°/⟨1012⟩, 34.8°/⟨1121⟩, 64.3°/⟨1122⟩ and 57°/⟨1011⟩ in the ruthenium samples. Figure 6 is the twin boundary map of ruthenium sintered for different times at 1250°C. For ruthenium sintered for 0.5 h, it can be seen there are a few 94.8°/⟨1012⟩ twin systems in the grain interior (Figure 6(a)). Figure 6(b) shows that for ruthenium sintered for 1 h, there are fewer twins in the grain interior, and the percentage of 94.8°/⟨1012⟩ twin
systems decreases while the other twin systems of 34.8°/\{11\overline{2}1\}, 64.3°/\{11\overline{2}2\} and 57°/\{10\overline{1}1\} increase as compared with Figure 6(a). The total twin density increases again, and the percentage of 94.8°/\{10\overline{1}2\} twin systems increases when sintering time reaches 2 h (Figure 6(c)). The total twin density decreases again with a sintering time of 4 h, although the percentage of 94.8°/\{10\overline{1}2\} twin systems increases to a maximum value of 72.1%. The statistics of twin boundaries in ruthenium samples are summarised in Table II. It can be seen that the longest 94.8°/\{10\overline{1}2\} twin was 42.6 μm for ruthenium sintered for 2 h. The total length of twin boundaries increases from ~0.5–2 h while the total length of twin boundaries achieves a maximum value of 64.3 μm with a sintering time of 2 h, then the value decreases to 44.2 μm with a sintering time of 4 h. In HCP titanium, the ratio of the lattice constants (c:a) is 1.587, which is similar to that of ruthenium (c:a = 1.582) (23). Previous research has shown that \{10\overline{1}1\} deformation twins occur during hot compression of titanium at 723 K and 0.1 s⁻¹ (24).

### 3.2 Hardness Characterisation

To examine the effect of microstructure on the mechanical properties of ruthenium, the Vickers
The microhardness of the samples was measured. The dependence of the hardness of the ruthenium samples on the sintering time is shown in Figure 7. The hardness increases at first and then it decreases with sintering time. The hardness of ruthenium sintered for 0.5 h was 447.2 HV, and it increased to a maximum hardness of 540.1 HV for ruthenium sintered for 1 h. The hardness decreased to 531.6 HV for ruthenium sintered for 2 h, then decreased to the minimum value of 407.8 HV for ruthenium sintered for 4 h. In a previous study of ruthenium hardness (3) the sintered tablets exhibited a hardness between 91 HV to 377 HV, while after hot working their hardness became 307 HV to 455 HV. The difference in the measurements may be explained by the fact that the samples in (3) were sintered without pressure and, as a result, their density was lower (9.69–11.88 g cm\(^{-3}\)).

### 3.3 Discussion

It was shown that the average grain size in the ruthenium samples is stable (~4–5 µm) and does not depend on the time of sintering at the process temperature of 1250°C (Figure 4). It seems that sponge particles could recrystallise under annealing at 1250°C for ~0.5–4 h, while this temperature is sufficiently low that the grains in the samples could begin growing during this short time. The initial powder size of materials may impact the grain size of the tablets during high pressure-high temperature sintering. For example, Shin et al. found that during the sintering of diamond there was no abnormal grain growth (AGG) for the initial powder size of 4 µm, while AGG happened for the initial powder size of 2 µm (25). Thus, the particle size of the present initial
ruthenium powder may be suitable for the present sintering conditions.

Early in the sintering process, after a sintering time of 0.5 h (Figure 5(a)), the pressure and high temperature caused particle rearrangement, sliding and metallurgical bonding. There were a few twins in some grain interiors suggesting the initial inhomogeneous deformation of ruthenium. The inhomogeneous state may be caused by different grain orientations in which some orientations deform easily or by areas with closely spaced grains and metallurgical bonding which deform first. As the sintering time reached 1 h (Figure 5(b)), the grains showed clean and uniform grain structure. In VHP samples, the particles were pressed together and kept in contact (26). Thus, there were more diffusion paths to promote atomic migration and induce sintering in multiple directions (27). With the appropriate pressure, temperature and holding time, voids were further crushed and ruthenium particles contacted and bonded with each other to form fully metallurgical bonding across grain boundaries. The density of ruthenium also increased slightly from 0.5 h to 1 h.

With the increase of sintering time to 2 h, ruthenium formed metallurgical bonding in almost the whole bulk material (Figure 5(c)). Defects such as twins and low-angle grain boundaries appearing inside grains point to some plasticity in the ruthenium samples. The total length of grain boundaries and twin boundaries reached a maximum value for a sintering time of 2 h, implying the maximum plastic deformation for
the present ruthenium sample. Thus, the density also reached a maximum value after sintering for 2 h. As sintering time further increased to 4 h (Figure 5(d)), there were fewer defects and boundaries inside the grains as compared with ruthenium sintered for 2 h, and the density also reached a minimum value in all samples sintered between ~0.5–4 h.

It is well known that annealing can induce crystal formation from such defects as dislocations and twins. Hence, the decreasing hardness of the samples sintered for 4 h could be caused by the annealing of twins which appeared in the material at earlier stages of sintering. During VHP, the ruthenium powders sustained the crushing of voids, formation of grain boundaries, grain growth, plastic deformation (formation of defects) and recovery of defects. As for the hardness of ruthenium with sintering time (Figure 6), the hardness increased first from 0.5 h to 1 h due to the crushing of voids and formation of tight boundaries. It was found that the maximum hardness was achieved for ruthenium sintered for 1 h, while the density reached its maximum value for ruthenium sintered for 2 h. According to Figure 1 and Figure 7, the samples’ density begins decreasing when sintered for 4 h. The hardness is prone to similar behaviour after processing for more than 0.5 h. This is normal behaviour for hardness because the twins’ density decreases after 4 h. It can be seen from the XRD pattern of ruthenium that the strongest peak is (0002) plane for ruthenium sintered for 1 h, while the strongest peak is (10\(\bar{1}1\)) plane for ruthenium sintered for 2 h (Figure 1). Since there was little difference in density and average grain size for the ruthenium samples sintered for 1 h and 2 h, the crystal orientation and defect density of ruthenium may play a role in the determination of hardness.

Ruthenium is a brittle metal due to its anisotropic HCP crystal structure that provides a limited number of independent slip systems, and twinning is an important deformation mode. Twinning has been observed in some metals and ceramics such as tungsten carbide, cubic boron nitrides and aluminium oxynitride ceramic during high-pressure and high-temperature sintering (28–30). Previous research has shown that deformation of ruthenium occurs by slipping on (10\(\bar{1}0\)) and twinning on (11\(\bar{2}1\), (11\(\bar{2}2\), (10\(\bar{1}1\) and occasionally (10\(\bar{1}2\) (3). In the present work, slipping and twinning occurred during VHP of ruthenium even at 1250°C, and the main twin system was 94.8°/(10\(\bar{1}2\)). The transition of the main twin system to 94.8°/(10\(\bar{1}2\)) may be attributed to the high temperature and pressure. Any HCP structure is anisotropic in comparison with a cubic structure. As a result, the total plasticity of an HCP-metallic single-crystal depends on its crystallographic orientation. It is significant for zinc and cadmium at room temperature because only the basal slip is active in these metals under these conditions. The orientation anisotropy of plasticity in titanium and zirconium is not so visible, insomuch as the prismatic slip’s contribution is added to the basal slip. The contribution of twinning to the total plasticity of an HCP-metal is minor, while twinning could influence its hardness and, perhaps, work-hardening. Also, it should be noted that a lot of twin systems exist in HCP-metals, which are known to be ductile and malleable materials. The low malleability of ruthenium is connected with the low cohesive strength of grain boundaries. In the case of PM ruthenium, it is due to brittle intergranular fracture, whose source is likely to be non-metallic impurities rather than its intrinsic properties. Further work still needs to be done to understand the relationship between impurity elements and the plasticity of ruthenium.

4. Conclusions

The VHP technique for the manufacture of ruthenium tablets based on powder metallurgical technology has been described. The method described here allows fine-grained metal with mechanical properties close to electron-beam melted ruthenium to be obtained.
Acknowledgments

The authors gratefully acknowledge support of the National Key Research and Development Program (No. 2017YFB0305503), International Science and Technology Cooperation Foundation of Yunnan Province, China (No. 2014IA037), and Yunnan Innovation Team Project (No. 2019HC024).

References

23. Z. Ahmadi, B. Nayebi, M. S. Asl and M. G. Karkoudi, *Mater. Charact.*, 2015, **110**, 77
The Authors

Renyao Zhang graduated from Yunnan Agricultural University, China, in June 2015 with a Bachelor’s degree in engineering. He is currently a Master’s student of Kunming Institute of Precious Metals, China, and conducts research under the guidance of Wen Ming. At present, the main research fields are precious metal sputtering targets.

Junmei Guo received her Master’s degree in Materials Science from Kunming Institute of Precious Metals. She has been working for Kunming Institute of Precious Metals since 1994. Her research interest is precious metal alloys and thin films.

Chuanjun Wang received his Master’s degree in Materials Science from Kunming Institute of Precious Metals. He has focused on the research and development of rare and precious metal sputtering targets for more than 11 years.

Limin Zhou graduated from Kunming University of Science and Technology, China, in 2000 with a Bachelor’s degree in engineering. He has worked for Kunming Institute of Precious Metals since 2005. His research interest is new preparation methods of precious metal alloys.

Ming Wen received his PhD degree in Materials Science from the School of Materials Science and Engineering of Shanghai Jiaotong University, China. He has worked for Kunming Institute of Precious Metals since he graduated from Shanghai Jiaotong University. His research interest is sputtering targets and related thin films. He has published more than 20 papers in Science Citation Index (SCI) journals recently.
Reviewed by Sara Gligoroska
Johnson Matthey, TIDZ Skopje 1, 1041 Ilinden, North Macedonia
Email: sara.gligoroska@matthey.com

Introduction

Into my hands came an exciting new book about space. “Spacecraft Thermal Control Technologies” is written by Professor Jianyin Miao, Qi Zhong, Professor Qiwei Zhao and Professor Xin Zhao. All the authors of this book are part of the Institute of Spacecraft System Engineering, China Academy of Space Technology (CAST), Beijing, China. Jianyin Miao is a head scientist of heat pipes at CAST and a Massachusetts Institute of Technology (MIT, USA) visiting professor, and is an academic leader for space thermal control technology at China Aerospace Science. Qi Zhong is a research fellow at CAST and his expertise is in the field of aerospace thermal control. Qiwei Zhao is a professor at CAST with expertise in the field of space thermophysics. Professor Xin Zhao has served as a chief designer of thermal control subsystems. He serves on the professional committee at CAST. He has received several national and ministerial awards for his work in this field. The series editor Peijian Ye, (China Academy of Space Technology, Beijing, China) is a Chinese aerospace engineer. He is a professor at the Beijing University of Aeronautics and Astronautics, China, and is a professor at the Harbin Institute of Technology, China. He is a research fellow and chief engineer at CAST. He is also the Chief Commander and Chief Designer of the Chinese Lunar Exploration Program. In his honour the inner main-belt asteroid 456677 Yepeijian, discovered by the Purple Mountain Observatory Near-Earth Object Survey Program at the XuYi Station, China, took his name in 2007.

This book is the first of a 10-part series called Space Science and Technologies. In this book you can find high quality data and some new findings in the area of spacecraft. It provides information for better and deeper understanding of China’s space industry.

Thermal Control Technologies

This book consists of seven main chapters: 'Introduction', 'Space Environment', 'Design of Spacecraft Thermal Control Subsystem', 'Typical Thermal Control Technologies for Spacecraft', 'Typical Thermal Control Design Cases of Spacecraft', 'Thermal Analysis Technology' and 'Spacecraft Thermal Testing'. The first chapter is the ‘Introduction’ written by Qi Zhong. This is the most important chapter because it introduces the subject matter and explains all the key words and basics. Part of the content in this chapter describes the mission of spacecraft thermal control, explains the main technology of thermal control and the main tasks of this field, and also lays out the requirements of this field.

The second chapter of this book is ‘Space Environment’. This chapter was written by Xin Zhao with Yanchao Xiang. In this chapter is information about the environment at the launching phase, Earth orbital thermal environment, thermal environment at re-entry and entry phase. The most interesting parts of this chapter are the
findings about the moon and planetary space environments, with details of the lunar, Mercury, Venus and Mars environments. The third chapter in this book is called ‘Design of Spacecraft Thermal Control Subsystem’, written by Xin Zhao, the same author as Chapter 2. In this chapter Xin used his experience and shared his knowledge about the ground, orbiting and landing phases. In this chapter are explained the basic principles of thermal control design and the design method of thermal control systems. The fourth chapter in this book is ‘Typical Thermal Control Technologies for Spacecraft’, written by Jianyin Miao, Weichun Fu and Hongxing Zhang. This chapter is focused mostly on heating and cooling technologies, with the main emphasis on heat transfer technology. Also as a part of this chapter are explanations about temperature measurement and control technology.

Conclusions

This book is very well written, containing informative details about the subject matter discussed in each chapter. The book is full of mathematical formulae, graphs and pictures. For me as a non-expert in space science, there were some things that required more time and research of the given matter to fully understand. But this book is definitely worth reading. The days spent reading this book were most interesting and I have learned much new information.

If you are a student in the field, scientist, professor or simply a fanatic for space and the universe this is the book that you need to read. We can be grateful to the people involved for sharing the vast knowledge they have gained in this area of work.

The Reviewer

Sara Gligoroska has a Bachelor’s degree in Pure and Applied Chemistry from the Faculty of Mathematics and Natural Sciences, Ss. Cyril and Methodius University in Skopje, North Macedonia. She works as a process engineer at Johnson Matthey. She is a space and universe enthusiast who is always interested in learning new things.
Johnson Matthey Launches New Platinum Group Metal Award Scheme

Emma Schofield, FRSC
Johnson Matthey, Blounts Court, Sonning Common, Reading, RG9 4NH, UK
Email: emma.schofield@matthey.com

Johnson Matthey is keen to encourage research into future applications of platinum group metals (pgms). As a global leader in sustainable technologies, our focus is on clean air, clean energy, healthcare and the efficient use of the planet's natural resources - and on the fundamental properties of pgms on which these applications depend.

Johnson Matthey's commitment to progress in platinum group metals technology is demonstrated by the launch of the new JM Platinum Group Metal Award Scheme in September 2021. This Scheme is a way for Johnson Matthey to give away pgm materials and salts to leading researchers engaged in inspiring science in sustainable technology areas. Each quarter, we will make a free gift of 5–10 g of a pgm material to the 10 to 15 applications to the Scheme that have the greatest potential to:

- Develop new markets for pgms
- Address current global challenges using pgm technology
- Substitute pgms into technologies where they can improve sustainability and performance
- Fill in gaps in our understanding of how pgms behave
- Further decrease the hazards of using sensitising pgm materials.

Regular readers of this journal may remember the original Johnson Matthey Metals Loans Scheme (1) which donated pgm salts to researchers for more than half a century (1955–2014). Sir Geoffrey Wilkinson used materials from the Johnson Matthey Loans Scheme for virtually all of his pgm research, which featured in around 200 of his 557 publications (2). The pgms from the Scheme contributed to the successful development of new, commercially successful technologies for catalysis, cancer treatment and pollution control among many others. Around 5000 journal publications feature pgm given by Johnson Matthey via the old Scheme.

Although the name has changed from Loan to Award Scheme, the best features of the scheme remain, including sending the end-of-life research samples back to one of Johnson Matthey’s UK centres to be collected for recycling. As the largest global refiner of secondary pgm materials, we have the processing capability in our Brimsdown and Royston facilities to upgrade the metal to 99.995% purity. Scheme metal will join the other pgms going round the endless recycling loop.
How to Apply

To apply for an award of pgm, visit the Johnson Matthey corporate website and search for "pgm award" or visit the link (3). Alongside a list of which pgm materials are available there is a link to a short form asking for some details of the applicant and the project. The JM Platinum Group Metal Award Scheme is open for application from any university or research institution globally, in any field where pgms have a crucial role.

References

4. “Securing Technology-Critical Metals for Britain”, University of Birmingham, UK, 2021

The Author

Emma Schofield is a Johnson Matthey Research Fellow based in the global Technology Centre near London, UK. She joined Johnson Matthey in 2004, enthusiastic about using inorganic chemistry to make the world a cleaner and healthier place in a company dedicated to creating the sustainable technologies of the future. As Recycling and Separation Technologies Research Manager, Emma focussed on understanding and improving the environmental impact of the industrial processes by which pgms and lithium ion battery metals are recycled. She was a Commissioner and contributor to the 2021 report “Securing Technology-Critical Metals for Britain” (4). She became a Johnson Matthey Research Fellow in January 2021, with the remit to promote the understanding and application of pgms in sustainable technologies globally.
“Space Robotics”

Reviewed by Wolfgang Kaltner
Johnson Matthey, Wardstraße 17, 46446 Emmerich am Rhein, Germany
Email: Wolfgang.Kaltner@matthey.com

Introduction
“Space Robotics” by Yaobing Wang belongs to the series Space Science and Technologies co-published by Beijing Institute of Technology Press, China, and Springer Nature Pte Ltd, Singapore. The Editor-in-Chief of the series, Peijian Ye, is Academician of the Chinese Academy of Sciences in Beijing and has published a collection of 10 volumes. This volume’s author, Yaobin Wang, is a research professor of Beijing Institute of Spacecraft System Engineering and Director of Beijing Key Laboratory of Intelligent Space Robotic Systems Technology and Applications. The book’s 363 pages provide a condensed combination of theory and practice as engineering guidance.

Starting from the particularity of space environment and application, the book discusses the theory and method of space robot design. The purpose is to provide the basic concepts and theories and introduce the basic methods and steps of engineering implementation of space robots.

Systems and Design
In the following review, the 16 chapters will be described briefly. If you are not planning to design a space robot now, you might want to start reading at Chapter 15.

Chapter 1 provides a very short introduction and gives a brief description of space robot classifications (for example on-orbit operation, planetary exploration) and basic composition of space robots, like the mechanical system, power system and perceptual system. Chapter 2 details kinematics and dynamics, the basis of analysing the characteristics and control with kinematic equations and the modelling process for dynamics, analytics and path planning (Figure 1). Chapter 3 refers to motion planning which is the process of generating the desired motion trajectory in the

Fig. 1. Relationships of robot links. Copyright (2021). Reprinted with permission from Springer
robot joint space or Cartesian space according to the mission target. Path planning is to find an optimal motion path from the starting point to the target in the working environment with obstacles, which involves using an algorithm to find the optimal or near-optimal collision-free path and controlling the robot to track the planned path.

Chapter 4 follows with implementation of motion control after motion planning. This chapter takes the single joint control as example to illustrate the motion control method of space robots. The objective of motion control is to achieve the tracking of the desired joint states (angle, speed) with two main methods: three-loop servo motion control and dynamic model-based motion control. Chapter 5 describes robot force control, a method of modifying the contact force between the robot and the environment by controlling the joint output. The main purposes are to protect the robot or the objects in contact. Several methods have been proposed, most of which fall into two categories, namely hybrid force and position control and impedance control.

Chapter 6 lists general processes of space robot system design including task requirement analysis, design feasibility study, preliminary system design and detailed system design. The tasks comprise designs of configuration, information flow, thermal, ergonomic and safety. Chapter 7 details the mechanical system, the core of a space robot, which is used to enable the motion functions. Its performance directly affects the application effect. Mechanical system design generally includes material selection (for example alloys), structural parts design, mechanism components design, lubrication in space and verification scheme design. The environmental conditions are the main constraints to the main components structure, joint, end effector and mobile wheel. Chapter 8 describes the control system consisting of command scheduling layer, motion planning layer and execution control layer. Furthermore, it gives information on the design of the control system (centralised control and distributed control) including the control system architecture and software.

Chapter 9 focuses on the space robot perception system, for example visual perception system and force perception system, but mainly describing visual parts, being optical assembly, structural assembly and electronic assembly. The main functions of the space robot visual perception system are to realise target detection, recognition and measurement (for example binocular, laser).

Chapter 10 provides details on the teleoperation system which is an interactive tool between human and space robot. The design requires processes to be developed for the following elements: operator, the core of the system, communications, environment and the human-robot interaction interface, which includes information receipt, simulation of the state of the robot and environment and signal conversion. The teleoperation system generally has the main functions of status feedback and instruction generation.

Chapter 11 explains the system verification methods. Comprehensive and rigorous ground verification prior to launch are important and are done via simulation and physical testing. Due to the complexity of the robot systems, the verification of all parameters is generally done via the design of a prototype using physical test verification, semi-physical simulation verification and mathematical simulation verification.

Chapter 12 is the first chapter mentioning a design example of a large space manipulator mainly used in the field of manned space exploration, such as the construction and operational support of a space station (for example Canadarm for the International Space Station (ISS)). It covers the engineering background, system design, mechanical system design, control system design, perception system design and design verification. Chapter 13 follows with a design example of a planetary exploration mobile robot, currently only in operation on Mars and lunar surfaces (Figure 2). The wheeled movement scheme requires extra design and verification of landing platform, suspension schemes, driving and steering schemes and obstacle avoidance systems. Chapter 14 provides another design example of a planetary surface sampling manipulator which is a space robot that performs sampling tasks on the planet surface, usually mounted on a planetary lander or a planetary rover to perform multi-point sampling and other operations. In this chapter the design and verification are introduced, detailing on performance, task, interface, system and constraints as well as joint design, arm design and sampler design.

Chapter 15 starts with the evolution of space robots in the 1980s before moving towards the current research and usage of space robots in space stations and planetary exploration. A list with brief information on on-orbit operation robots and planetary exploration is provided. Chapter 16 is the final chapter and focuses on future prospects of space robots which will be developed with regard to their tasks of manned spaceflight, deep space exploration and planetary round trips.
exploration and on-orbit services. Driven by the mission demands, space robots will integrate the latest achievements in the development of science and technology and will be constantly improved in form, function and performance to meet the needs of space missions. Some new concepts include soft robots, flying robots, space cloud robots, space multi-robot systems and artificially intelligent space robots.

Conclusions

The book is recommended for university students, researchers and engineers in the related fields. Most of the book focuses on theory, definitions and mathematical expressions, making the book a helpful tool for design of a space robot from the theoretical side. I would have expected details on currently operating space robots. In almost 400 pages only two tables provide a very basic overview of on-orbit operation and planetary exploration robots. Chapters 15 and 16 were most interesting as they go beyond the theoretical background, describing the current state and future prospects of space robots.

The Reviewer

Wolfgang Kaltner is Head of Strategic Hydrogen in Fuels and Energy, Catalytic Technologies at Johnson Matthey, Germany. He is a chemical engineer and holds a PhD in Technical Chemistry. His interest in hydrogen and novel technologies has shaped his professional career.
Surface science methodologies, such as reflection-absorption infrared spectroscopy (RAIRS) and temperature programmed desorption (TPD), are ideally suited to studying the interaction of molecules with model astrophysical surfaces. Here we describe the use of RAIRS and TPD to investigate the adsorption, interactions and thermal processing of acetonitrile and water containing model ices grown under astrophysical conditions on a graphitic dust grain analogue surface. Experiments show that acetonitrile physisorbs on the graphitic surface at all exposures. At the lowest coverages, repulsions between the molecules lead to a decreasing desorption energy with increasing coverage. Analysis of TPD data gives monolayer desorption energies ranging from 28.8–39.2 kJ mol\(^{-1}\) and an average multilayer desorption energy of 43.8 kJ mol\(^{-1}\). When acetonitrile is adsorbed in the presence of water ice, the desorption energy of monolayer acetonitrile shows evidence of desorption with a wide range of energies. An estimate of the desorption energy of acetonitrile from crystalline ice (CI) shows that it is increased to \(\sim 37\) kJ mol\(^{-1}\) at the lowest exposures of acetonitrile. Amorphous water ice also traps acetonitrile on the graphitic surface past its natural desorption temperature, leading to volcano and co-desorption. RAIRS data show that the C≡N vibration shifts, indicative of an interaction between the acetonitrile and the water ice surface.

### 1. Introduction

Dust grains have been found in a number of astrophysical regions including the interstellar medium (ISM, the space between the stars), comets and planetary atmospheres (1, 2). In many of these regions, the grains are covered in multi-component molecular ices. The exact constituents of these ices are region dependent, but the main constituents are usually water and methanol (see for example Pontopiddan et al. (3)). Astrophysical ices also contain smaller amounts of volatile molecules such as carbon monoxide, methane and carbon dioxide and so called complex organic molecules (COMs) (4) (in astronomical terms, COMs are defined as carbon-containing molecules with six or more atoms).

Surface processes, such as addition reactions (5, 6) and thermal and energetic processing (see for example (7–13) and references therein) have been shown to be crucial in the formation of many of the molecules found in these ices and in the gas phase (2). Ultrahigh vacuum (UHV) surface science techniques, such as RAIRS and TPD, have been shown to play an important role in understanding the complex chemistry taking place on grain surfaces.

Approximately 1% of the total mass of the ISM is attributed to dust grains (1, 14). These grains are primarily carbonaceous and silicaceous in nature (1, 2) and, due to the cold temperatures in the ISM (20–30 K), are covered in molecular ices. Over 200 molecules have been identified in the gas phase in the ISM to date, ranging from small diatomics such as hydrogen (15) and carbon monoxide (16) to larger COMs such as HC\(_{11}\)N (4, 17). Laboratory surface science investigations have shown that model dust grains play a critical role in the formation of many of these species. For example, it is now widely agreed that H\(_2\) forms in...
the ISM via the recombination of H atoms on dust grain surfaces (see for example (5) and references therein). Laboratory investigations have also shown that atom and radical addition reactions on grain surfaces are the main formation route for a range of molecules of varying complexity, such as water (18, 19), CO$_2$ (20) and methanol (6, 21). The formation of more complex species, such as hydrocarbons, alcohols and nitriles, has also been demonstrated upon irradiating adsorbed ices with low energy protons, ions and electrons (see for example (9, 22–30) and references therein).

In addition to reactive processes, thermal processing also plays a very important role as it leads to the sublimation of species from ices into the gas phase. Once in the gas phase, molecules are available to react to form other species. Hence it is important to understand the desorption of molecules from the ices. Surface science studies of the sublimation of model ices are therefore crucial for understanding and modelling such processes. A number of laboratory studies have used TPD to investigate the thermal induced sublimation of a large number of molecules from dust grains analogous to those found in the ISM. For example, desorption has been investigated from metallic surfaces (see (31, 32) for examples), from carbonaceous surfaces (see (33, 34) for examples), from silicate surfaces (see (32, 34) for examples), from forsterite (see (35) for example) and from bulk-like ice surfaces (see (36, 37) for examples). Through analysis of TPD (33, 38–43) and infrared data (44–47), kinetic parameters of molecules have been determined and incorporated into models in order to accurately describe the desorption of molecular ices from dust grains on astrophysically relevant timescales (48–50).

While interstellar ice is comprised of multiple components, laboratory studies often investigate the desorption of pure molecular ices adsorbed on a variety of metallic, graphic and silicate substrates in order to provide the basis for understanding more complex ice systems (31, 41, 51, 52). Water is the dominant component of interstellar ices, comprising ~60–70%, depending on the region. Water ice exhibits a range of phases determined by its growth conditions (53). At temperatures below 130 K, water exists as amorphous solid water (ASW) (54, 55). Two phases of ASW have been identified: a high-density amorphous phase at temperatures ~10 K and a low-density, less porous, phase between 35 K and 65 K (55). As water ice is heated, a phase change occurs from ASW to CI as the temperature increases from 130 K to 160 K (53, 56, 57). The different water ice phases have been shown to have a significant impact on the adsorption and desorption of other molecular species co-deposited on top of or within water ice (33, 37, 58–61).

To illustrate the use of UHV surface science investigations in understanding the adsorption and surface chemistry of ices on dust grain analogue surfaces, this paper describes the adsorption of acetonitrile (CH$_3$CN) (Fig. 1(a)) and water-containing ices on a graphic dust grain analogue surface, highly oriented pyrolytic graphite (HOPG). HOPG is considered to be a suitable analogue of carbonaceous dust grain surfaces and has been used previously in a range of studies of astrophysical relevance (33, 62, 63). Here we study the adsorption and desorption of acetonitrile and water-containing ices of various configurations, shown in Fig. 1(b). Acetonitrile-HOPG and acetonitrile-water interactions have been characterised and kinetic parameters for desorption have been determined in order to provide a detailed overview of the desorption behaviour and the effect of water on the acetonitrile. We also show how these data can be used to describe desorption under relevant astrophysical conditions. To the best of our knowledge, the adsorption and desorption of acetonitrile and water has not been described in detail on a graphic surface previously.

Acetonitrile is the simplest organic nitrile and is significant in astrophysical terms due to the C≡N group, which plays an important role in amino acid formation and hence potentially in the prebiotic chemistry necessary for life (64). It has been detected in a number of astrophysical environments such as protoplanetary disks, Titan’s atmosphere, comets and the ISM (65–79). Previous studies of acetonitrile adsorption on a range of substrates have demonstrated the formation of weakly bound physisorbed monolayer and multilayer ices (31, 80–85). Spectroscopic

---

Fig. 1. Schematic showing: (a) the structure of the acetonitrile (CH$_3$CN) molecule; and (b) the different acetonitrile and water ice configurations investigated in this study.
investigations have characterised the nature and orientation of acetonitrile on the surface and in the gas and liquid phases (7, 80–82, 84, 86–89). Infrared spectra, recorded as a function of annealing temperature, show a change in band shape and intensity, indicating a phase change of amorphous to crystalline acetonitrile at a temperature between 95–110 K (7, 84, 90–94). TPD and infrared spectroscopy have also been used to study the interactions of acetonitrile with water and heavy water (D₂O) in layered and mixed ice complexes (83, 95–97). Non-thermal processing of acetonitrile ices, using electrons, photons and high energy ions, has also been investigated (7, 84, 98).

2. Methodology

In order to understand the desorption of molecules from model dust grains at the low pressures and temperatures relevant to astrophysical conditions, experiments were carried out using a stainless steel UHV chamber with a base pressure of <2 x 10⁻¹⁰ mbar. The methodologies used here have been described previously (99, 100). Briefly, the HOPG sample was cooled to a base temperature of 29 K. Acetonitrile (Sigma Aldrich, purity 99.9%) and deionised water were purified by a series of freeze-pump-thaw cycles prior to deposition. A range of ice configurations were grown by background dosing, including pure acetonitrile; layered acetonitrile/water ices; and acetonitrile:water mixtures, as shown in Figure 1(b). Two types of layered ices were investigated, consisting of acetonitrile on CI and on ASW. CI and ASW were grown as described previously (99, 100). Exposures are measured in Langmuir (L_m) where 1 L_m = 1 × 10⁻⁶ mbar s.

TPD data were recorded with a linear heating rate of 0.50 ± 0.01 K s⁻¹. A range of mass fragments were monitored for acetonitrile and water. The mass fragments for each species exhibited identical behaviour, therefore only the most intense fragments are shown here: m/z = 41 for acetonitrile and m/z = 18 for water. RAIR spectra consist of the co-addition of 256 scans at a resolution of 4 cm⁻¹. RAIRS annealing experiments were carried out by increasing the temperature of the sample and holding it at the target temperature for 3 min, before cooling and recording a spectrum. For all TPD and RAIRS experiments, multiple data sets are recorded to ensure reproducibility of results.

3. Results and Discussion

3.1 Temperature Programmed Desorption for Pure Acetonitrile on Highly Oriented Pyrolytic Graphite

Although pure acetonitrile is not found in astrophysical environments, studying pure ices is useful in order to determine the detailed physical and chemical behaviour of the ice and to provide a comparison with the behaviour in the presence of water ice. Figure 2 shows TPD data recorded following the adsorption of increasing amounts of acetonitrile on HOPG at 29 K. At the lowest exposures investigated, 0.5–2 L_m (Figure 2(a)), a decreasing peak temperature with increasing exposure is observed. This can be assigned to initially repulsive interactions between acetonitrile molecules on the HOPG surface. This effect has been seen for ultra-thin acetonitrile films adsorbed on SiO₂ (84) and for other molecules such as benzene on HOPG (38, 101). Behaviour of this type could also be explained by a distribution of binding sites with different adsorption energies, however this is unlikely in this case since HOPG is a very uniform surface.

For acetonitrile exposures between 3 L_m and 7 L_m (Figure 2(a)) the TPD data show an
approximately constant peak temperature with increasing exposure, which is characteristic of first-order desorption of molecular acetonitrile, and indicates that monolayer desorption occurs over this range of exposures. The low temperature desorption, at approximately 127 K, and the approximately constant peak temperature indicate that acetonitrile forms a physisorbed monolayer on the HOPG surface at the intermediate exposures shown in Figure 2(a). The spectra seen in Figure 2(a) are in contrast to those seen for thin acetonitrile films adsorbed on SiO$_2$ (8, 84), where the acetonitrile peak temperature decreases with increasing coverage for all monolayer exposures. This difference is likely a consequence of the more uniform HOPG surface compared to the more uniform SiO$_2$ surface studied by Abdulgalil et al. (8, 84).

TPD data for increasing exposures of acetonitrile on HOPG from 7–100 L$_m$ can be seen in Figure 2(b). The data clearly show a single desorption feature which increases in temperature with increasing exposure. Traces in Figure 2(b) also show shared leading edges. These observations are indicative of the desorption of acetonitrile multilayers following zero-order kinetics. This is in good agreement with previous studies of multilayer acetonitrile adsorbed on a range of surfaces (7, 31, 82–84, 95).

Kinetic analysis of the TPD data shown in Figure 2 was performed using methods described previously (33). TPD data can be described by the Polanyi-Wigner equation (Equation (i)) where $r_{des}$ is the rate of desorption, $\theta$ is the coverage, $t$ is the time, $A$ is the pre-exponential factor, $n$ is the order of desorption, $E_{des}$ is the activation energy for desorption, $R$ is the gas constant and $T$ is the temperature of the substrate.

$$ r_{des} = -\frac{d\theta}{dt} = A\theta^n \exp\left(\frac{-E_{des}}{RT}\right) $$

Analysis using the Polanyi-Wigner equation enables us to obtain $n$, $E_{des}$ and $A$. The order of desorption, $n$, can be obtained from rearrangement of Equation (i) as shown previously (33). This gives the order of desorption from a plot of $\ln[I(T)]$ (where $I(T)$ is the recorded mass spectrometer signal at temperature $T$) as a function of $\ln[\theta_{rel}]$ (where $\theta_{rel}$ is the relative coverage, given by the integrated area under the TPD curves) at a fixed desorption temperature. Figures 3(a) and 3(b)

![Fig. 3](https://example.com/fig3.png)

Fig. 3. (a) An example of a plot used to determine the order of multilayer desorption at a fixed temperature of 131 K; (b) an example of a plot used to determine the order of desorption for monolayer desorption of acetonitrile, at a fixed temperature of 125 K; (c) a plot used to determine the desorption energy of 100 L$_m$ of acetonitrile adsorbed on HOPG.
show examples of such plots for acetonitrile at fixed desorption temperatures of 125 K (monolayer order) and 131 K (multilayer order) respectively. Plots such as this are produced for a range of temperatures using data on the leading edge of the TPD curves; so called leading edge analysis (33). Average values for the order of the monolayer and multilayer desorption can then be obtained from these plots.

The order of desorption for monolayer acetonitrile was found to be 0.89 ± 0.05. The order for multilayer acetonitrile desorption was determined to be 0.08 ± 0.07. These values are as expected for monolayer and multilayer desorption of physisorbed species (33). These desorption orders were obtained for exposures of acetonitrile from 3–100 L\(_m\). The lowest exposures (0.5–2 L\(_m\)) were omitted from the analysis of the order of desorption as they show behaviour associated with repulsive interactions and hence do not give meaningful data for the desorption order.

Once the desorption order has been determined, a plot of \(\ln[I(T)]–\ln[\theta_{rel}]\) versus \(1/T\) can be used to determine \(E_{des}\) (33). The gradient of this plot is equal to \(-E_{des}/R\). An example of this plot for a 100 L\(_m\) exposure of acetonitrile is shown in Figure 3(c). Desorption energies can be determined for each exposure of acetonitrile to show the variation in desorption energy as a function of exposure, as seen in Figure 4.

The inset to Figure 4 clearly shows a decreasing desorption energy with increasing exposure for the very lowest exposures of acetonitrile on HOPG. Following this, the desorption energy increases to the multilayer desorption energy value. A decrease in desorption energy with increasing exposure was also seen by Abdulgalil et al. for acetonitrile adsorption on SiO\(_2\) (84). The average value of the desorption energy of multilayer acetonitrile is determined to be 43.8 ± 1.7 kJ mol\(^{-1}\). For exposures less than 5 L\(_m\), assigned to monolayer desorption, the desorption energy ranges from 28.8–39.2 kJ mol\(^{-1}\). The monolayer energy determined here is somewhat lower than that determined by Abdulgalil et al. (84) (35–50 kJmol\(^{-1}\)) and by Bertin et al. (95) (44.4 ± 2.8 kJ mol\(^{-1}\)) for monolayer desorption from SiO\(_2\) and α-quartz respectively. This is most likely due to the different binding energy of acetonitrile with the carbonaceous HOPG surface compared to that on a silicate surface. The multilayer desorption energy determined here is in reasonable agreement with that determined by Abdulgalil et al. (84) (38.2 ± 1 kJ mol\(^{-1}\)).

Once the desorption order and activation energy for desorption have been determined, it is possible to obtain values for the pre-exponential factor for desorption, \(A\) (33). The average pre-exponential factor for the desorption of monolayer acetonitrile from HOPG was determined to be \(3.4 \times 10^{15} \pm 0.5 \text{ s}^{-1}\). This value is as expected for the desorption of a monolayer species from a surface. The value obtained for multilayer desorption of acetonitrile from HOPG is \(1.4 \times 10^{12} \pm 0.3\ \text{molecules m}^{-2} \text{ s}^{-1}\). This value is in good agreement with that previously obtained for the desorption of acetonitrile from SiO\(_2\) (84).

### 3.2 Reflection-Absorption Infrared Spectroscopy of Pure Acetonitrile on Highly Oriented Pyrolytic Graphite

RAIR spectra for acetonitrile adsorbed on HOPG at 29 K are shown in Figure 5. The top spectrum shows that recorded upon adsorption at base temperature. The spectrum shown is for the adsorption of 80 L\(_m\) of acetonitrile on HOPG. Adsorption from 0.5–80 L\(_m\) is not shown here, but shows that bands increase in intensity with increasing amount of acetonitrile on the surface. No frequency shifts are observed for increasing amounts of acetonitrile. This indicates that physisorption is taking place, as already shown by the TPD spectra in Figure 2. The assignments of the bands shown in Figure 5 are given in Table I and are made by comparison with the literature. Bands in the high wavenumber region are assigned to the symmetric and antisymmetric methyl group.

![Figure 4. The calculated desorption energy of acetonitrile adsorbed on HOPG as a function of exposure, for the TPD data in Figure 2. The inset shows the lowest exposures of acetonitrile, from 0.5–10 L\(_m\).](https://doi.org/10.1595/205651321X16264409352535)
stretching modes at 3001 cm\(^{-1}\) and 2941 cm\(^{-1}\) respectively. The C≡N stretching mode is observed at 2253 cm\(^{-1}\) and is the most intense band observed in the spectrum. In the lower wavenumber region, a band at 1373 cm\(^{-1}\) is assigned to the symmetric methyl group deformation mode, while bands at 1412 cm\(^{-1}\) and 1448 cm\(^{-1}\) are also assigned to methyl group deformation modes. The band at 1045 cm\(^{-1}\) is assigned to the methyl group rocking mode (not shown) and a further mode at 914 cm\(^{-1}\) (also not shown) is assigned to the C–C stretching mode.

**Figure 5** also shows the results of annealing the adlayer of acetonitrile adsorbed on HOPG at 29 K. The acetonitrile was annealed in 10 K increments up to its desorption temperature. No changes were observed in the spectra until 100 K and hence these spectra have been omitted from **Figure 5**. Following annealing to 100 K, there is an increase in intensity of the C≡N stretch and a small decrease

---

**Table I Reflection-Absorption Infrared Spectroscopy Assignments for Acetonitrile**

<table>
<thead>
<tr>
<th>Assignment</th>
<th>HOPG at 29 K</th>
<th>Multilayer on gold at 90 K (95)</th>
<th>SiO(_2) at 15 K (84)</th>
<th>Water/silver at 124 K (83)</th>
<th>Water/platinum(100) at 120 K (97)</th>
<th>Gas phase (86)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(v_5), CH(_3) d-stretch</td>
<td>3001</td>
<td>3000</td>
<td>3001</td>
<td>3001</td>
<td>3001</td>
<td>3009</td>
</tr>
<tr>
<td>(v_1), CH(_3) s-stretch</td>
<td>2941</td>
<td>2939</td>
<td>2941</td>
<td>2940</td>
<td>2941</td>
<td>2954</td>
</tr>
<tr>
<td>(v_2), CN stretch</td>
<td>2253</td>
<td>2251</td>
<td>2252</td>
<td>2271/2251</td>
<td>2250</td>
<td>2266</td>
</tr>
<tr>
<td>(v_6), CH(_3) d-deformation</td>
<td>1448</td>
<td>1455</td>
<td>1449</td>
<td>1454</td>
<td>1455</td>
<td>1448</td>
</tr>
<tr>
<td>(v_6), CH(_3) d-deformation</td>
<td>1412</td>
<td>1419</td>
<td>1410</td>
<td>1419/1409</td>
<td>1422</td>
<td>1410</td>
</tr>
<tr>
<td>(v_3), CH(_3) s-deformation</td>
<td>1373</td>
<td>1378</td>
<td>1375</td>
<td>1378</td>
<td>1378</td>
<td>1390</td>
</tr>
<tr>
<td>(v_7), CH(_3) rock</td>
<td>1045</td>
<td>1036</td>
<td>1040</td>
<td>1038</td>
<td>1039</td>
<td>1041</td>
</tr>
<tr>
<td>(v_4), CC stretch</td>
<td>914</td>
<td>917</td>
<td>920</td>
<td>919</td>
<td>–</td>
<td>920</td>
</tr>
</tbody>
</table>

*All values are given in wavenumber, cm\(^{-1}\)*
in the wavenumber of this band to 2251 cm\(^{-1}\). This change is accompanied by intensity changes and frequency shifts for other bands in the spectrum. For example, the methyl group stretching mode at 2941 cm\(^{-1}\) moves downwards to 2939 cm\(^{-1}\) following annealing to 100 K; the band at 1448 cm\(^{-1}\) sharpens and increases in wavenumber to 1454 cm\(^{-1}\); and the band at 1045 cm\(^{-1}\) decreases in wavenumber to 1038 cm\(^{-1}\). Further annealing to 110 K shows an increase in intensity of all of the bands in the spectrum, along with a splitting of the bands at 1410 cm\(^{-1}\) and 1373 cm\(^{-1}\). No further changes in the spectrum are observed and all modes have disappeared from the spectrum by 130 K. The lack of bands in the spectrum following annealing to 130 K is evidence for desorption of acetonitrile by this temperature. This temperature is slightly lower than that observed in the TPD spectra, seen in Figure 2, due to the different nature of heating in both cases.

The observed changes in the RAIR spectra following annealing to 110 K can be assigned to the crystallisation of acetonitrile that occurs upon annealing. Acetonitrile crystallisation has been studied in detail by Hudson (92) and the spectra shown in Figure 5 are in good agreement with the high temperature crystalline phase described by Hudson. The crystallisation of solid phase organic species has been observed previously for a range of molecules (42, 92, 100, 102). Recording infrared spectra for ices adsorbed on model grain surfaces helps to allow the identification and assignment of spectra recorded in astrophysical environments. For example, the presence of acetonitrile has been observed in Titan’s atmosphere and hence accurate infrared spectra can help with assignment of observational data (7, 67, 92, 93).

### 3.3 Acetonitrile Adsorbed in the Presence of Water Ice

As described in the introduction, astrophysical ices contain large amounts of water ice, with the exact amount and ice phase depending on the region of space. Given that astrophysical ices are primarily composed of water ice, it is necessary to investigate the interaction of astrophysically relevant molecules with various configurations of water ice as shown in Figure 1(b).

Figure 6 shows TPD data resulting from the adsorption of thin films of acetonitrile in the presence of water ice in different configurations. It is clear from Figure 6 that the presence of ASW has a significant effect on the desorption behaviour of acetonitrile compared to pure acetonitrile ices (Figure 2). Even at the lowest exposures, three features are observed in the TPD data.

The highest temperature species at approximately 158 K can be assigned to the co-desorption of acetonitrile with the bulk water ice. This assignment is confirmed by the fact that this peak has the same desorption temperature as the main water desorption. This observation of co-desorption has also been seen for other molecules (100, 102, 103) and occurs as the molecules become trapped in the bulk of the water ice when the ASW-CI phase transition occurs (31, 103).

The sharp acetonitrile desorption feature observed at approximately 146 K is assigned to volcano desorption of acetonitrile that becomes trapped in the pores of the water ice as the ASW to CI phase transition occurs at ~145 K. The observation of the volcano and co-desorption peaks provides evidence that the acetonitrile likely diffuses into the water ice surface, prior to the ASW to CI phase
transition occurring. Volcano and co-desorption have previously been seen for a number of molecules, both smaller volatiles (31, 33, 53, 104) and larger organic species (32, 50, 99, 100), adsorbed on and in ASW. The lowest temperature acetonitrile desorption peak seen in Figure 6(c) can be assigned to the desorption of acetonitrile directly from the amorphous water ice surface.

Significant desorption is only seen directly from the ASW surface once the pores of the ASW are saturated and hence this lowest temperature peak only becomes significant for the higher exposures of acetonitrile on ASW. Further increasing the amount of acetonitrile on the ASW leads to the formation of multilayer acetonitrile with desorption behaviour following that of the pure acetonitrile shown in Figure 2.

In contrast to the behaviour of acetonitrile on ASW (Figure 6(c)), adsorption on CI shows simpler desorption behaviour (Figure 6(b)). There are no desorption features that can be assigned to volcano or co-desorption, as expected since the water ice in Figure 6(b) is grown in the crystalline phase. Instead, desorption directly from the CI surface is the only desorption peak observed in the spectrum. Figure 7 shows a comparison between the desorption of acetonitrile from the bare HOPG surface (Figure 7(c) and 7(d)) and from the CI surface (Figure 7(a) and 7(b)). There is clearly a difference in the desorption behaviour of acetonitrile bonded to CI compared to acetonitrile bonded to HOPG. In particular, for the lowest exposures, equivalent amounts of acetonitrile desorb at a higher temperature from CI than from HOPG. For example 2 L\textsubscript{m} of acetonitrile desorbs from HOPG at a temperature of ~126 K compared to a temperature of ~139 K from CI. In addition, the peak profiles for acetonitrile desorbing from CI are considerably broader compared to those seen for desorption directly from HOPG.

The broader peak profile for acetonitrile desorbing from CI suggests that there is a range of desorption energies and a distribution of binding sites for the acetonitrile on the CI surface. These observations are in agreement with previous investigations of acetonitrile on CI by Bertin et al. (95) which have also been assigned to the observation of a range of desorption energies for acetonitrile on the CI surface. As seen in Figure 7(a), as the amount of acetonitrile on the CI surface increases above 3 L\textsubscript{m} there is evidence for an additional peak growing into the TPD at lower temperature. Figure 7(b) shows that this feature can be assigned to the growth of multilayers of acetonitrile on the CI surface as also seen in Figure 7(d) for acetonitrile adsorbed directly on HOPG.

Leading edge analysis can also be applied to the TPD curves shown in Figures 6(b) and 7(a) to provide an estimate of the desorption energy of acetonitrile from the CI surface. Analysis of the TPD

![Fig. 7. TPD data showing a comparison of the desorption behaviour of equivalent doses of acetonitrile: (a) low exposures of acetonitrile, from 1–5 L\textsubscript{m} on top of CI; (b) higher exposures of acetonitrile, from 4–10 L\textsubscript{m} on top of CI; (c) low exposures of acetonitrile, from 1–5 L\textsubscript{m} adsorbed directly on HOPG; (d) higher exposures of acetonitrile, from 4–10 L\textsubscript{m} adsorbed directly on HOPG](image-url)
curves for 1 \text{L}_m and 2 \text{L}_m of acetonitrile adsorbed on CI, with an assumed desorption order of one, give desorption energies of 36.8 ± 0.8 kJ mol\(^{-1}\) and 36.6 ± 0.7 kJ mol\(^{-1}\) respectively. Note that, as already discussed, the shape of the TPD curves for monolayer acetonitrile desorbing from CI indicates that there are a range of desorption energies dictating the desorption. These desorption energy values hence give an estimate of the increase in the desorption energy from the CI surface, compared to the HOPG surface, and do not give the full range of desorption energies across all binding sites. Analysis of multilayer TPD data for acetonitrile adsorbed on CI give the same desorption energies as already determined for pure acetonitrile, as expected. For exposures ≥3 \text{L}_m, Figure 7(b) shows that the additional low temperature feature assigned to the growth of multilayers is already growing into the TPD curves. Hence it is not appropriate to use a desorption order of one to obtain desorption energies for these spectra. An attempt was also made to determine desorption energies for acetonitrile monolayers desorbing from the ASW surface. However, the complexity of the data are such that it was not possible to determine reliable energies of desorption for this system. Nonetheless, a comparison can be made with the data for monolayer acetonitrile on CI (Figure 7(a) and 6(c)), which show that the monolayer on both water ice surfaces shows similar features. Hence, it is expected that the monolayer acetonitrile on ASW desorbs with a wide range of energies, and from a broad range of binding sites. As for desorption from CI, the desorption energy from the ASW surface is higher than from HOPG, and is likely to be around ~37 kJ mol\(^{-1}\), as determined from leading edge analysis of the data resulting from desorption of acetonitrile from CI.

The desorption energy values for 1 \text{L}_m and 2 \text{L}_m of acetonitrile on CI are significantly higher when compared to equivalent exposures adsorbed directly on HOPG (shown in Figure 4) and correspond to a stronger binding energy of the acetonitrile on the CI surface. This can be assigned to an interaction between the C≡N of the acetonitrile and the water ice, as confirmed by RAIR spectra (shown later). This observation of a higher binding energy on CI is in agreement with previous observations (95).

Figure 6(a) also shows the desorption of acetonitrile from mixed ices, formed by co-deposition of acetonitrile and ASW. It is clear from Figure 6(a) that the behaviour of the mixtures is very similar to that of acetonitrile adsorbed on ASW (Figure 6(c)). This behaviour of acetonitrile in the presence of water ice is consistent with that observed for other organic molecules that have weaker interactions (when compared with strongly hydrogen-bonding species such as methanol) with water ice such as methyl formate (103) and ethyl formate (99). This behaviour occurs as the molecule forms a weak interaction with the polar water ice surface, as shown by the different desorption energy when compared to that on HOPG.

Figure 6 also shows that the acetonitrile has an effect on the temperature of the ASW-CI phase transition. Figure 6(c) shows the volcano desorption peak decreasing in temperature with increasing acetonitrile exposure on the ASW surface. The same effect is also seen for mixed ices (Figure 6(a)) where the ice containing a higher percentage of acetonitrile shows a lower temperature volcano desorption. This effect has been reported previously for species that strongly hydrogen bond to water such as methanol (105). It has also been seen for more weakly bonded species that do still interact with water, such as ethyl formate adsorbed in the presence of water ice (99), and provides evidence for an interaction between acetonitrile and water.

Further evidence for an interaction between acetonitrile and water ice is shown in Figure 8, which shows the C≡N stretch of acetonitrile in different ice configurations at 29 K. From Figure 8 it is clear that in the presence of ASW, either in a

![Fig. 8. RAIR spectra showing the C≡N stretching region for acetonitrile adsorbed in different ice configurations at 29 K. The spectra result from the deposition of 20 \text{L}_m acetonitrile on HOPG, on ASW and on CI and from the deposition of a 29% acetonitrile:ASW mixture.](image-url)
layered or mixed ice configuration, the C≡N stretch has a different line shape when compared to that observed for pure acetonitrile on HOPG. For the mixed ice, the C≡N stretch shifts to 2266 cm\(^{-1}\), compared to 2253 cm\(^{-1}\) for the pure ice, showing evidence of a direct interaction between the acetonitrile and water ice. In contrast, the C≡N stretch for acetonitrile adsorbed on top of ASW shows features for both the pure acetonitrile (2253 cm\(^{-1}\)) and for the acetonitrile bonded to water ice (2266 cm\(^{-1}\)). Acetonitrile bonded to CI has the same vibrational frequency as that seen for pure acetonitrile. This is unsurprising since the spectra shown in Figure 8 are for the adsorption of 20 L\(_m\) of acetonitrile in different ice configurations. At this exposure, TPD spectra shown in Figure 7 also show that acetonitrile on CI and on HOPG exhibit similar behaviour. The sensitivity of our RAIRS experiment is less than that of the TPD experiment and hence it is not possible to record RAIR spectra for the very lowest exposures of acetonitrile on the surface. 

Figure 9 shows the results of annealing an acetonitrile adlayer adsorbed on top of ASW (Figure 9(a)) and a mixed acetonitrile water layer (Figure 9(b)), focusing on the C≡N region of the spectrum. This is the only spectral region that shows appreciable differences when compared with spectra that result from annealing a pure acetonitrile ice (Figure 5). For acetonitrile adsorbed on top of ASW, annealing the ice leads to the appearance of a high wavenumber shoulder at 2266 cm\(^{-1}\) (Figure 9(a)), initially becoming more prominent following annealing to 110 K. The main C≡N stretch at 2253 cm\(^{-1}\) also sharpens and shifts down in wavenumber slightly to 2251 cm\(^{-1}\). This effect was also seen for the annealing of pure acetonitrile ice (Figure 5) and can be assigned to the crystallisation of the acetonitrile layer adsorbed on top of the ASW. Subsequent annealing of this system to 130 K leads to a complete change in the RAIR spectrum. The sharp feature at 2251 cm\(^{-1}\) disappears from the spectrum and the only band that remains is a very broad feature centred at 2266 cm\(^{-1}\).

Comparing the spectrum at 130 K in Figure 9(a) with the spectrum at 130 K for the annealing of pure acetonitrile ice (Figure 5) shows that this peak can be assigned to acetonitrile trapped within water ice. Annealing of pure acetonitrile ice to 130 K (Figure 5) leads to complete desorption and no peaks are observed in the RAIR spectrum. However, TPD data for acetonitrile adsorbed on top of ASW show the presence of volcano and co-desorption peaks due to acetonitrile trapped within the ASW structure. Hence, the infrared band seen at 130 K following the annealing of the layered ice can be assigned to acetonitrile trapped within the water ice structure. This band occurs at the same wavenumber as that seen for acetonitrile in a mixed ice at base temperature (Figure 8), further confirming the assignment of this peak to acetonitrile trapped within, and interacting with, water ice. Further annealing to 140 K leads to complete desorption of the acetonitrile from the surface. Note that TPD data for the desorption of acetonitrile from the layered ice show slightly higher desorption temperatures than 140 K. This is due to the different heating methods used in the infrared and TPD experiments.

Figure 9(b) shows RAIR spectra resulting from the annealing of a mixed ice. For this ice, there is no evidence of crystallisation of acetonitrile. This is unsurprising since the acetonitrile is within the water ice matrix and hence cannot nucleate to form a crystalline structure. As seen in Figure 9(b), no changes are observed in the RAIR spectrum until the ice has been annealed to above 100 K. Following annealing to above 100 K the spectrum gradually changes to give a very broad feature with bands centred around 2266 cm\(^{-1}\) and 2280 cm\(^{-1}\). Whilst the 2266 cm\(^{-1}\) band has already been assigned, it is not clear what the exact origin of the band at 2266 cm\(^{-1}\) is. However, it is likely that

![Image](https://doi.org/10.1595/205651321X16264409352535)
this also occurs due to an interaction between the acetonitrile and the water ice, although the exact assignment of the band requires further investigation. As for the acetonitrile on ASW, there is clear evidence for the presence of acetonitrile trapped within the water ice as bands are observed up to 140 K in the spectrum, which is considerably higher than seen for pure acetonitrile.

4. Simulations of Desorption Under Astrophysical Conditions

Data of the type described here can be used to simulate desorption under ‘real’ astrophysical conditions, that is with appropriate ice thicknesses and relevant heating rates. Heating rates in astrophysical environments are considerably slower when compared to those in the laboratory. A typical heating rate in an astrophysical environment is around 1 K century\(^{-1}\) (106), compared to 0.5 K s\(^{-1}\) used in the experiments described here. The thickness of astrophysical ices depends on the region, however an ice thickness of 0.3 µm is considered to be appropriate for star-forming regions (48).

The desorption energies derived from our TPD data shown in Figure 2 have been used to determine the desorption temperature of acetonitrile ices under astrophysically relevant heating rates. It is the desorption temperature, not the desorption energy, that is generally put into astrophysical models and hence it is necessary to determine the desorption temperature under astrophysically relevant conditions. Our simple model uses the Polanyi-Wigner equation (Equation (i)) to simulate desorption at a range of heating rates for an ice thickness consisting of \(3.42 \times 10^{21}\) molecules m\(^{-2}\) of pure acetonitrile. This surface coverage is that calculated for an ice thickness of 0.3 m, using a density for solid acetonitrile of 0.778 g cm\(^{-3}\) as determined by Hudson (92).

Figure 10 shows desorption profiles for pure acetonitrile at a number of heating rates ranging from 0.5 K s\(^{-1}\) (the laboratory heating rate) down to 0.01 K year\(^{-1}\) (an astronomically relevant heating rate). As can clearly be seen, the peak temperature for the desorption of acetonitrile decreases considerably as the heating rate decreases, with a peak temperature of \(\sim 90\) K being seen for the slowest heating rate. In addition, as the heating rate decreases the width of the desorption peak (in terms of temperature) decreases, with the slowest heating rates showing a relatively sharp desorption event happening at the peak temperature. Note that these simulations have been performed using a desorption order of zero and incorporating a relevant pumping speed in order to simulate TPD profiles. The pumping speed is scaled in accordance with the scaling of the heating rate to allow the production of TPD peaks at different heating rates. Determination of the desorption temperature under astrophysically relevant heating rates is essential to allow the incorporation of the results of TPD experiments such as those described here into astronomical models of star and planet formation. For example, data of this sort have been used to describe desorption of ices in star-forming regions (48). It is only with appropriate laboratory experiments that accurate values of desorption energies can be incorporated into astronomical models.

5. Conclusions

This paper has described the adsorption and desorption of acetonitrile from model astrophysical ices adsorbed on a carbonaceous dust grain analogue surface, HOPG. RAIRS and TPD data have shown that acetonitrile physisorbs on the HOPG surface at all exposures. At the lowest exposures, repulsions between the adsorbed acetonitrile molecules are observed, which lead to an initially decreasing desorption energy with increasing exposure. Subsequent adsorption leads first to standard monolayer behaviour, and
then to the formation of multilayers of acetonitrile on the surface. Water ice, either in the form of ASW or CI, has a substantial effect on the adsorption and desorption of acetonitrile, with ASW trapping the acetonitrile beyond its natural desorption temperature. Characterising the trapping and desorption behaviour of molecules in interstellar ices is very important for providing astronomers with accurate information for astrophysical models based on experimental data. For example, previous studies have classified the desorption behaviour of small molecules as carbon monoxide-like, water-like or intermediate (31) and a more recent study has extended these classifications to COMs (103), by predicting the trapping and desorption of molecules based on the way that they interact with water ice. Classification of the desorption behaviour of COMs then allows astronomers to correctly model the sublimation of a wide range of molecules including those for which laboratory data does not currently exist. Based on its behaviour as described here, acetonitrile can be classified as a complex intermediate species (103). This means that acetonitrile traps in ASW and desorbs mainly via volcano desorption as ASW undergoes a phase change. However, there is also an interaction between the molecule and the water ice surface giving rise to desorption directly from the water surface which has different characteristics when compared to desorption directly from the dust grain analogue surface. Furthermore, acetonitrile also has an effect on ASW itself as observed for other similarly classified molecules such as methyl formate (103) and ethyl formate (99).

RAIRS can also be used to provide information about the interactions between the ice components. Data of this type can be used to compare with observational data, and hence help to identify the environment in which a molecule is found in space (107). For example, the data reported here clearly show that the band profile of the C≡N stretch of acetonitrile changes markedly in the presence of ASW in a mixed ice.

Acknowledgements
The Engineering and Physical Sciences Research Council (EPSRC) are acknowledged for a studentship for Emily Rose Ingman, funded by the Doctoral Training Grant (DTG) allocation to the University of Sussex, UK. Jack Fulker is acknowledged for help with the RAIR spectrum for layered acetonitrile/CI ices. Daren Burke is acknowledged for help with figures and general discussions.

References
63. L. Horneckær, A. Baurichter, V. V. Petrunin, D. Field and A. C. Luntz, Science, 2003, 302, (5652), 1943


80. F. Koubowetz, J. Latzel and H. Noller, J. Colloid Interface Sci., 1980, 74, (2), 322


86. F. W. Parker, A. H. Nielsen and W. H. Fletcher, J. Mol. Spectrosc., 1957, 1, (1–4), 107


100. S. A. Ayling, D. J. Burke, T. L. Salter and W. A. Brown, RSC Adv., 2017, 7, (81), 51621


The Authors

Emily Rose Ingman graduated from Aberystwyth University, UK, in 2018 where she obtained a Masters degree in Astrophysics. She is currently a member of the Brown Group at the University of Sussex, UK, where she is studying for her PhD in Astrochemistry. The focus of the PhD is to investigate the surface science reactions of model interstellar ices on dust grains.

Amber Shepherd is currently studying for her masters degree in Chemistry at the University of Sussex. She is working within the Brown group to complete her final year project which investigates the interactions and desorption behaviour of acetonitrile in the presence of water and deuterated water ices on model interstellar dust grains.

Wendy Brown is a Professor of Physical Chemistry and Head of Department at the University of Sussex, where she has been since 2013. Her current research interests focus on surface science processes of relevance to astrophysical processes. Over her career to date she has undertaken UHV surface science investigations on a range of surfaces including metals, oxides and graphitic surfaces.
In the medium temperature range for thermoelectric applications, the n-type half-Heusler TiNiSn is very promising. Unfortunately, there is a major barrier related to scaling up as several weeks annealing time is required for the synthesis of TiNiSn. A mixture of arc-melting, ball-milling, and spark plasma sintering was used in this work to synthesize TiNiSn. High-purity, high-density, and fine grains with diameters of up to 30 mm were obtained in the samples. To improve the thermoelectric properties of TiNiSn, copper was added, which achieved, at 773 K, a maximum figure of merit of 0.6. The possibility of industrial scaling-up has been opened up by the fast and scalable synthesis of TiNiSn.

In this study, based on first principles, the aim is to consider scandium copper chalcogenides (ScCuX₂) to evaluate lattice thermal conductivity, transport properties, the thermoelectric figure of merit and structural stability. Evaluations include Debye temperatures plus transverse and longitudinal sound velocity in ScCuX₂ compounds along with phonon lifetimes, mean free paths and group velocities. Among the three ternary compounds in the findings, when the majority charge carriers are holes having a carrier concentration of 1019 cm⁻³, ScCuSe₂ has the highest value of dimensionless figure of merit of 0.65 at high temperatures (1000 K).

Terahertz pulsed imaging was used to investigate liquid transport kinetics of α-alumina powder compacts formed under different sintering conditions and compaction forces. There was an impact on the water ingress rate due to the surface properties and microstructure characteristics of the alumina compacts. It was shown that the mass transport characteristics were consistent with Darcy flow. The hydraulic radius was calculated based on the transport data.

The work undertaken looks to reduce deactivation rate during Fischer-Tropsch synthesis (FTS) through the possibility of passivating a Co/γ-Al₂O₃ catalyst by atomic layer deposition (ALD). Different numbers of ALD cycles (3, 6 and 10) were used with three samples of the reference catalyst. The results showed a shell of the passivating agent (Al₂O₃) growing around the catalyst particles which did not affect the properties of passivated samples below 10 cycles though it hindered catalyst reduction. Catalytic tests at 50% and 60% CO conversion were conducted. The technical feasibility of this technique was proven in FTS as 3 to 6 ALD cycles reduced Co/γ-Al₂O₃ deactivation.
Monitoring the Process of Formation of ZnO from ZnO₂ using in situ Combined XRD/XAS Technique


The thermal decomposition of zinc peroxide to zinc oxide is reported here. XAS and in situ combined XRD were used to conduct the study. From the data extracted comparison was made of XRD and XAS with TGA. This enabled the nature of the conversion of ZnO₂ to ZnO to be followed. Using a temperature range of 230–350°C seems to show, prior to forming an ordered ZnO material, that a poor crystalline ZnO is formed. White line intensity decreases in the zinc K-edge XANES plus lower coordination numbers from analysis of the zinc K-edge data of ZnO heated at 500°C, compared to bulk ZnO, suggests significant defects in the system for the ZnO produced.

Dense Pt Nanowire Electro catalyst for Improved Fuel Cell Performance Using a Graphitic Carbon Nitride-Decorated Hierarchical Nanocarbon Support


Engineering supported-platinum nanowire (NW) electrocatalysts with a high platinum content for the cathode of hydrogen fuel cells is presented in this innovative strategy. This uses g-CN@MPC formed by the deposit of graphitic carbon nitride (g-CN) onto 3D multimodal porous carbon (MPC) as an electrocatalyst support. Improved performance was observed with the g-CN@MPC-supported high-content platinum catalysts in relation to their counterparts. These were MPC, VC and g-CN@VC-supported platinum NW catalysts. Also for the benchmark catalyst the conventional platinum nanoparticle catalyst (Pt(20 wt%)NPs/VC (Johnson Matthey)) was used. At a very low cathode catalyst loading (≈0.1 mgs⁻¹ cm⁻²), a high PEM fuel cell power/performance is demonstrated by the g-CN-tailored high-content platinum NW (≈60 wt%) electrocatalyst.

The Role of Chromium in Iron-Based High-Temperature Water-Gas Shift Catalysts under Industrial Conditions


This study investigated chromium promotion of iron oxide based water-gas shift catalysts prepared via calcination/coprecipitation. The catalysts were aged for four days under realistic conditions. XRD and Mössbauer spectroscopy results demonstrated that chromium is incorporated in the calcined haematite (α-Fe₂O₃) precursor. Chromium doping was shown to affect the activation of α-Fe₂O₃. Increasing the chromium doping led to enhanced CO conversion and to an increased Fe³⁺:Fe²⁺ ratio in octahedral sites of magnetite. Computational studies modelling the chromium and vacancy-doped magnetite structures supported the results of the Mössbauer spectra. The study concluded that the bulk structure of an in situ prepared chromium-doped high-temperature water-gas shift catalyst is best expressed as a partially oxidised chromium-doped magnetite phase.

Atomic Layer Deposition with TiO₂ for Enhanced Reactivity and Stability of Aromatic Hydrogenation Catalysts


ALD was used to apply an ultrathin coating of TiO₂ on a conventional supported palladium catalyst in a scalable powder coating process, with the aim of enhancing hydrogenation performance. The TiO₂-coated catalyst displayed significant gains in the conversion of multiple aromatic molecules, and such enhancements were maintained when the coating synthesis process was scaled from 3 g to 100 g. Computational modelling, XAS and XPS results attributed the activity enhancement to ensemble effects resulting from partial TiO₂ coverage of the palladium surface. Further investigation showed that the TiO₂ coating improved the catalyst’s hydrothermal stability, tolerance toward sulfur impurities in the reactant stream and thermal stability.

Platinum Incorporation into Titanate Perovskites to Deliver Emergent Active and Stable Platinum Nanoparticles


A resilient catalyst was achieved using a perovskite system incorporating 0.5 wt% platinum into the support and its subsequent conversion through exsolution. Barium platinate, which is a thermally stable platinum oxide precursor, was utilised to preserve the platinum as an oxide throughout the solid-state synthesis. An equilibrated and uniform structure with active emergent platinum nanoparticles strongly embedded in the perovskite surface was attained by tailoring the procedure. In comparison to conventionally prepared platinum catalysts, the structure demonstrated greater stability and CO oxidation activity. Further investigations studied ammonia slip reactions, CO and NO oxidation and diesel oxidation catalysis.
Operando Neutron Scattering: Following Reactions in Real Time Using Neutrons


In this study, quasielastic neutron scattering was used to observe reaction progress in the complexation of NiCl$_2$ with 2,2′-bipyridine. A high-resolution engineering diffractometer was used to induce strain in the aluminosilicate framework, and thus observe water adsorption in chabazite with time resolution. The results from this work highlight the recent advances and future possibilities of using neutron probes for the observation of realistic catalytic reactions as they proceed.

Roles of the Basic Metals La, Ba, and Sr as Additives in Al$_2$O$_3$-Supported Pd-Based Three-Way Catalysts


A variety of spectroscopic and kinetic studies were conducted to investigate the roles of typical basic metal additives (barium, lanthanum and strontium) in palladium-based TWC systems. Metallic Pd$^0$ species on La/Al$_2$O$_3$ were electron-deficient, whereas those on Ba/Al$_2$O$_3$ and Sr/Al$_2$O$_3$ supports were more electron-rich compared to those on pristine Al$_2$O$_3$ (Figure 1). During NO reduction reactions, Pd/La/Al$_2$O$_3$ exhibited a lessened CO poisoning effect. Further studies using both powdered and monolithic catalysts showed that Pd/Ba/Al$_2$O$_3$ exhibited the highest activity for the oxidations of CO and C$_3$H$_6$, and Pd/La/Al$_2$O$_3$ promoted the catalytic reduction of NO most efficiently. The authors concluded that the optimal metal additive for a palladium-based TWC should be ascertained by the specific application.

Packing Simulations of Complex-Shaped Rigid Particles using FDEM: An Application to Catalyst Pellets


The effects of friction, geometric features and energy dissipation parameters on the bulk properties of rigid pellet packs were estimated by employing a new component of the combined finite-discrete element method (FDEM). The numerical simulations of packing of glass beads, trilobe pellets and cylindrical catalyst supports were confirmed to match the corresponding emergent bulk properties attained from X-ray CT scans. This study is the first to confirm the applicability of FDEM based methods to the simulation of this class of multi-body problems.

Fig. 1. Reprinted from Y. Jing et al., J. Catal., 2021, 400, 387, Copyright (2021), with permission from Elsevier
Editorial team

Manager Dan Carter
Editor Sara Coles
Editorial Assistant Yasmin Stephens
Senior Information Officer Elisabeth Riley

Johnson Matthey Technology Review
Johnson Matthey Plc
Orchard Road
Royston
SG8 5HE
UK
Tel +44 (0)1763 253 000
Email tech.review@matthey.com

www.technology.matthey.com