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VIRTUAL ISSUE 6 ‘SOUTH AFRICA: PGM EXTRACTION TO APPLICATIONS’ DECEMBER 2012

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The earliest authenticated scientific report of the occurrence of platinum in rocks from the Bushveld Complex, South Africa, appears to be that of William Bettel on 10th November 1906. Thereafter, prospecting of the chromite-rich rocks for platinum proved frustrating. It is argued that the resurgence of interest by Dr Hans Merensky in 1924 resulted from his realisation that newly panned platinum had a grain size different from that in the chromite layers and indicated a different source rock, which he promptly located as the Merensky Reef.

The story of the discoveries by Dr Hans Merensky (Figure 1) of the platinum-rich pipes and the Merensky Reef itself in 1924 has been well documented (1). However, the events preceding the discoveries have not been summarised. In the probable centenary year of the first report of platinum in the Bushveld, it is appropriate to review those events from 1906 to 1924.

Bushveld Platinum Reported on 10th November 1906

In geology it is risky to claim a date for the “first” documentation of any event. However, it is suggested that for the occurrence of platinum in the Bushveld Complex, this can reasonably be considered to have been a report (2) by William Bettel on 10th November 1906 in an article in South African Mines, Commerce and Industries, a weekly journal then published in Johannesburg.

Platinum in South Africa

To cover all possibilities concerning first dates, a reference to “platina” (the old name for platinum) should be mentioned. A specimen, together with assorted other geological samples, was displayed on Church Square, Pretoria, by a prospector, Dick Hart. It was collected from an area of ~ 130 km by 75 km around Pretoria. The event was recorded in the Pretoria newspaper Die Volkstem on 27th July 1885 (cited in (3), p. 52). There is no reason to doubt the prospector’s identification (“platina” had little value then), or the probability that it came from the Bushveld Complex, but the display had no impact on the mining community.

To return to Bettel: he was the chief chemist at the Robertson gold mine in Johannesburg at the time. His story begins in 1890 when he analysed a “black sand” concentrate from a stamp battery (used for crushing gold ore) from a gold mine in Klerksdorp, 100 km southwest of Johannesburg (a mere four years after the first discovery of the gold reef in Johannesburg). Bettel found the concentrate to contain “silver, gold, platinum and iridium (with osmium)”. Hence, the presence of the platinum group elements in South Africa in minor amounts was well established by the end of the nineteenth century.

In Situ Platinum

Bettel stated in his article that he “recently” (i.e. before November 1906) analysed half-a-dozen...
samples of chromite-bearing rock, which he described as “olivine gabbro”, and had found them to contain platinum. He regarded this documentation as marking the first instance of platinum in situ in South Africa. Bettel referred to the samples as being from the Transvaal, but did not have permission to divulge exact details of the locality. His description is sufficiently precise that these samples can safely be considered to be from the Bushveld Complex. This report therefore represents the first published documentation of platinum in the Bushveld Complex.

Russian Analogies

Bettel commented on analogies with the Russian occurrences of platinum, which were the major source of platinum at that time. Thus began a mistake or digression by South African geologists to which Percy Wagner referred. Wagner wrote (4): “The professional geologist made only one mistake. He followed too closely the experience gained in the Urals, where platinum is always associated with chromite”.

The Russian deposits were all alluvial, but the source rock was known to be chromitite, occurring in peridotite (an olivine-rich rock). The rocks were all uneconomic to mine. It was only the decomposition of the peridotite and chromitite, and upgrading of the dense minerals by river action, that made the alluvial Russian occurrences payable. Indeed, so closely was the Russian analogue followed, that once Merensky found the first outcrops of dunite pipes and the Merensky Reef in the eastern Bushveld in 1924, he focused a great deal of his attention on exploring alluvium in the confluence of two perennial rivers downstream from the outcrop. He incorrectly thought that there might be major concentrations of easily worked alluvial platinum derived from these outcrops.

Chromitite in the Bushveld

The South African geologists followed this Russian model closely and began investigations into the chromite-rich rocks of the Bushveld Complex. By contrast, “the rocks associated with the chromite were neglected” (4). Geologists of the Geological Survey of South Africa, Wagner’s employer at the time, made a study of the chromite-rich rocks of the Bushveld Complex. Hall and Humphrey reported the occurrence of platinum in these rocks in 1908 (5), a publication that is often quoted as the first reference to platinum in the Bushveld Complex. Fifteen years later, Wagner (6) reviewed all the information available on platinum in chromite and concluded “that it would never pay to work the chromite rock for that metal [platinum] alone”. The highest grade quoted was about 2 g t⁻¹.

During the period 1906 to 1923, it can be assumed that it was not only the Geological Survey that was actively evaluating the platinum potential in chromite. It would appear that considerable exploration was also being undertaken. The extent of this can only be guessed, but the biography of Dr Hans Merensky by Olga Lehmann, “Look Beyond the Wind” (7), contains an interesting few sentences. Referring to the period before 1924, Lehmann wrote “Many prospectors, including Merensky, found copious chromite…”, but there had been “four or five disastrous platinum discoveries of former years that had not covered their finders in glory”. If Merensky had been involved in previous unsuccessful exploration projects in the eastern Bushveld, why should he try to raise money again in 1924 for yet another prospecting campaign?

“Look Beyond the Wind”

The above review is based entirely on published documents, but I now speculate on why Merensky would contemplate a subsequent exploration project when the previous attempts had been unsuccessful. Admittedly, the first platinum mine in South Africa had just opened in 1923, near Naboomspruit, 150 km away, but Merensky knew well that the host to the platinum there was in quartz veins, geologically apparently totally unrelated to the Bushveld Complex. That was therefore not the incentive.

To get inside Merensky’s mind, I must refer to another incident related by Olga Lehmann (7). Merensky had been contracted by a major mining house in Johannesburg to evaluate a reported gold
discovery in Madagascar. Several consultants joined ship in July 1905 en route to Madagascar, and were shown an area in which gold had been found. Merensky and others retraced this gold with their pans through several streams and small pits. Then Merensky “looked beyond the wind”. He turned in the opposite direction from his hotel and began panning other streams. He again found gold and realised that the area which the consultants were meant to investigate had been salted (illegal enrichment of an ore in an area or sample to be assayed). How? Merensky recognised that the gold grains panned in the area being promoted and the gold grains he found from elsewhere were of different shapes, and that the associated dense minerals in his pan were different in the two localities. Sadly, salting was not an unknown activity in those days, but Merensky had looked beyond the obvious, used his mineralogical acumen and recognised the fallacy!

Merensky’s 1924 Exploration

The next question is how the Madagascar salting incident relates to Merensky’s 1924 visit to the eastern Bushveld. Previous exploration projects had focused on the chromitite layers. A great deal is now known about the platinum group minerals and their sizes in the chromitite layers, especially the Upper Group 2 chromitite layer. Their typical size is from 2 to (rarely) 30 μm (8). Merensky would have known that panning in the field from crushed chromitite yielded very little platinum, because it was so fine grained that it was washed out of the pan. Had he ever found any in his pan, it would have been almost submicroscopic. Presumably, platinum grades based on panning would not have agreed with chemical analyses of chromite ore samples. Lest modern mineralogists question the accuracy of such comparative tests, it should be noted that Merensky stated in his early reports that panning and chemical analysis of samples from the Merensky Reef gave remarkably similar grades.

In 1924, Andries Lombaard, a farmer in the eastern Bushveld, sent Merensky an “aspirin bottle” containing a white concentrate, panned from a stream on his farm, Maandagshoek. Merensky had it chemically analysed to confirm that it was platinum. Merensky evidently used his experience in Madagascar to good effect. He looked at the particle size of the platinum group minerals in the concentrate, and realised that they were enormous by comparison with everything that had been found in the chromitite layers. Merkle and McKenzie (8) reported typical grain sizes from the Merensky Reef as 10–200 μm, and Wagner (9) reported a grain of 0.9 cm from the dunite pipes.

In 1998 the present author revisited the area on Maandagshoek from where Lombaard panned platinum. Some soil samples were analysed by Anglo Platinum (10). Subsequently some German colleagues undertook a mineralogical study of the same area and found grains of various platinum group minerals in excess of 0.2 mm or 200 μm size (11) (see Figure 2). Merensky performed both studies in a matter of a day in 1924, and came to the right conclusion. Merensky realised that the platinum grains on Maandagshoek were totally different from those found in the chromitite layers, and indicated a different source rock. The material was also coarse enough to be separable mechanically (the main extraction process in those days), with very good recovery of up to 85% (7). He commenced his often-documented exploration with Lombaard. This ultimately had enormous consequences for the world platinum industry.

Sceptics may claim that my suggestion cannot be verified. None of the reports written by Merensky himself contain any interpretation or rationale to his prospecting, merely very factual statements. However, the many and varied discoveries made by Merensky and documented by Olga Lehmann (7) demonstrate his remarkably astute geological sense. His appreciation of the significance of grain size would have been an obvious parameter in his prospecting skills.

References

3 J. Gray, “Payable Gold: An Intimate Record of the History of the Discovery of the Payable Witwatersrand Goldfields and of Johannesburg in
Grains of platinum group minerals panned from the farm Maandagshoek in the eastern Bushveld Complex, where the Merensky Reef was found in 1924. These photographs were reported by Oberthür et al. (11), and are reproduced here by permission of the Editor of The Canadian Mineralogist. Note the scale, indicating that these are large grains (by platinum group mineral standards), and are very different from anything found in chromitite layers.

Fig. 2(a) Grain (a) is a well-rounded grain of platinum-iron alloy; its shape suggests that it has been transported over a long distance and rolled about in a river system.

Fig. 2(b) Grain (b) is a near-perfect cube, also of platinum-iron alloy. The corners of grain (b) are still sharp, suggesting a very local derivation.

Fig. 2(c) Grain (c) has been cut through its centre and is photographed through a microscope. Its overall rounded shape suggests long transportation. It is made of several discrete minerals. The platinum alloy is labelled Pt-Fe, and other minerals are labelled as follows: 1: laurite (RuS2); 2: an unnamed mineral (Pd11Te2As2); 3: palladoarsenide (Pd2As); 4: sperrylite (PtAs2); 5: irarsite (IrAsS).

Grains of platinum group minerals panned from the farm Maandagshoek in the eastern Bushveld Complex, where the Merensky Reef was found in 1924. These photographs were reported by Oberthür et al. (11), and are reproduced here by permission of the Editor of The Canadian Mineralogist. Note the scale, indicating that these are large grains (by platinum group mineral standards), and are very different from anything found in chromitite layers.

1886–1887", Central News Agency, Johannesburg, 1937, 286 pp
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The Author

Grant Cawthorn comes from England. He has degrees in geology from Durham and Edinburgh Universities. After a post-doctoral fellowship in Newfoundland, he now teaches igneous petrology in the Department of Geology at the University of the Witwatersrand, South Africa. His main interest is in the formation of the Bushveld Complex with its vast reserves of platinum, chromium and vanadium. His post at the University is supported by the mining industry, and he holds the title of the Platinum Industry’s Professor of Igneous Petrology.
There are enough platinum group element deposits in the Bushveld Complex in South Africa to supply world demands for many decades or even a century using current mining techniques. Demonstrated reserves and resources published by mining companies make detailed calculations up to a maximum of about twenty years ahead, but there is abundant and adequate geological evidence that these deposits continue far beyond where mining companies have proven according to rigorous international reporting codes. For each 1 km of depth into the Earth in the Bushveld Complex there is in the order of 350 million oz of platinum. For comparison, annual production of platinum from the Bushveld Complex currently is only around 5 million oz. The distinction between ‘reserves’, ‘resources’ and ‘deposits’ is also explained in this article.

Introduction
In the minerals sector of world economics, the Bushveld Complex in South Africa (Figure 1) is renowned for its overwhelming deposits of platinum group elements (PGE) and chromium (over 80% of the world’s deposits of each according to Crowson (1)). Inevitably, from time to time, the question is raised as to how reliable those estimates are. The occurrences of all other mineral deposits are scattered around the world in an erratic way. Each deposit type has well-understood geological processes that operated to form them, but those processes have operated usually all over the world and in many cases throughout long periods of Earth’s 4.6 billion-year history, so that most commodities are mined in many different countries. Therefore, the PGEs, and especially platinum itself, are unusual in that they are largely concentrated in a single location.

Mining companies may only publish ‘reserves’ and ‘resources’ of platinum. However, as discussed below (see box) (2, 3), this figure represents only what has been rigorously quantified in the short- to medium-term mining plans of these companies, and excludes...
Fig. 1. Map of the Bushveld Complex in South Africa, showing the eastern, western and northern limbs. Major towns and cities are marked in red, operating platinum mines and projects currently underway are shown in green.
all the geologically known extensions of these deposits for which an in-depth (and expensive) evaluation is not justified. Current legally enforced definitions operative in several countries, including the USA, Canada, Australia, the UK and South Africa, define ‘reserves’ and ‘resources’ quite precisely, and exclude what geologists know to be identified deposits. In the case of those deposits in the Bushveld Complex there is simply no need to rigorously quantify them at this point in time, because there are adequate proven reserves already identified.

A number of estimates of the potential deposits of the PGE in the Bushveld Complex have been published in scientific journals over the last thirty years, and the quoted numbers have not changed significantly. A summary of these compilations is presented in Table 1 (1, 4–7). These reports have come mainly from South African-based geologists, and their figures have been reproduced or validated by independent organisations such as the United States Geological Survey (USGS), that have staff qualified to make critical assessments of these estimates.

The Geology of the Bushveld Complex

Before discussing how these estimates are calculated, it is worth considering the origins and geology of the Bushveld Complex. The economic potential of many ore deposits is difficult to evaluate, but this is not so in the case of the Bushveld ores. The Bushveld Complex (see Figure 2) is an enormous irruption of magma (molten rock) sourced deep within the Earth. The extent of the magma flow was at least 300 km in diameter. In the order of 1 million km³ of magma was emplaced in a (geologically) very short period of time. As this enormous volume of Bushveld magma slowly cooled, different minerals began to solidify and accumulate in thin, parallel layers at the bottom of this huge magma ocean. The maximum thickness ultimately was about 8 km.

Most minerals in the Bushveld Complex have no economic importance, but two types are important here: chromite and the sulfide group of minerals. Both of these mineral types concentrate the PGE. The first economically important discovery of platinum in the Bushveld Complex was found in a single...
layer, associated with the sulfides, that we now call the Merensky Reef after its discoverer, Dr Hans Merensky (8). Figure 3 shows a specimen of a Merensky Reef section. The distribution of the PGE vertically through the Merensky Reef layer is somewhat variable, but mining companies would aim to extract a layer in the order of 1 m in thickness that contains the majority of the total PGE. Lower-grade ore below and above this zone has to be left behind as it is not economical to process. For that reason it is usually excluded from any resource calculations.

Even before the Merensky Reef was discovered, the presence of platinum in chromite-rich layers in the Bushveld Complex was quite well known, but never found to be economic. There are a number of these chromitite layers in the Bushveld Complex, some reaching up to 1 m in thickness. They contain up to 3 grams per tonne (g t⁻¹) of PGE, often with quite high proportions of rhodium and lesser amounts of iridium and ruthenium. One layer, called the Upper Group 2 (UG2) chromitite layer, is a possible hybrid of the sulfide- and chromite-hosted reefs. The distribution of the PGE associated with the chromitite layers is sharply controlled by the chromite. There is essentially no PGE above or below the chromitite reef, and so the mining operations and resource calculations are much easier to define.

Assaying of a borehole intersection of the Merensky Reef and/or UG2 Reefs usually involves taking several consecutive lengths, each about 20 cm long, which are individually analysed, so that the best mineralised, 1 m-thick interval, especially for the Merensky Reef,
can be identified. Often two or three deflections are drilled for each borehole. This involves putting a wedge into the hole some 20–30 m above a reef intersection, and redrilling. This produces another section of reef within a metre of the first (mother) hole, providing more analytical and statistical data without the cost of drilling long, deep holes. Since many boreholes are drilled to intersect the reef at up to 2 km depth such deflections provide more information extremely cheaply. Over the many years of mining, confidence in the statistical variability of reef intersections permits reliable information on predicted grade. Until ten years ago most such exploration was based around the major existing mines in the western Bushveld. Since then, because of the rise in the platinum price (9), much exploration has been undertaken on areas in the eastern Bushveld, at great depths in established mining areas, and also where there are geological complications, for both the Merensky and UG2 Reefs. Two such examples of the latter would be around the Pilanesberg intrusion in the west, and near the Steelpoort fault in the east.

**Estimating Reserves and Resources**
Paradoxically, although there are now more data available than previously, the ability to publish estimates
of the platinum content of the Bushveld Complex is much more restricted. When the first estimates were calculated (Table I) they included predictions, projections and interpretations of geological continuity which are geologically plausible. Now, based on statutory resource codes, it is necessary to report all information only in terms of ‘reserves’ and ‘resources’, and whether proven or inferred. All the early calculations would have contained ore that would fall far outside what is now considered ‘inferred’. No exploration or mining company is going to expend unnecessary effort on proving deposits that might become mineable only a long way into the future. As a result, it appears as if the currently quoted platinum deposits of the Bushveld Complex are less than they actually are (compare Table II with Table I), purely because only ‘reserves’ and ‘resources’ may be reported and geologically known deposits are formally excluded by statutory codes. Even with this limitation, the ‘reserves’ and ‘resources’ reported by the four major mining companies in South Africa amount to at least 1200 million oz of PGE of which more than 50% is platinum (Table II).

From a purely geological perspective, we can make the following calculation from the following simple assumptions. We can assume the thickness of mineable Merensky and UG2 Reefs to be 0.8 m each. Geological maps show the two reefs to occur at outcrops with a strike length of about 100 km in both eastern and western limbs, giving a measure of the horizontal extent of the reef. We know that the typical dips of the reefs are less than 15º, so the reef can be mined for 4 km down the dip before a vertical depth...
of 1 km is reached. The densities of Merensky and UG2 Reefs are 3.2 t m$^{-3}$ and 4.0 t m$^{-3}$ respectively (7). We can take a conservative grade of 2 g t$^{-1}$ (0.06 oz t$^{-1}$) of extractable platinum. Simple multiplication of these figures (strike length along outcrop $\times$ distance into the Earth $\times$ thickness $\times$ density $\times$ grade, using appropriate units) yields 350 million oz of platinum per km depth (see box below). I use this method of presenting the information (in oz per km depth) because it is not known what mining depths may be ultimately viable. This simple calculation ignores what are called geological losses (assorted features such as faults and potholes, as described by Vermaak and van der Merwe (7)).

Taking a mining depth to 2 km, and adding what might be present in the Platreef which occurs in the northern limb of the Bushveld Complex (see Figure 2), gives the rounded figure of 800 million oz of platinum, similar to that reported by Crowson (1) in Table I. For comparison, the annual refined production of the major platinum producers in South Africa is shown in Table II, and amounts to only around 9 million oz of PGE, of which less than 5 million oz are platinum.

Table II  
PGE Reserves, Resources and Annual Refined Production Reported by the Major Platinum Mining Companies in South Africa for 2009$^a$

<table>
<thead>
<tr>
<th>Company</th>
<th>Reserves, million oz</th>
<th>Resources$^b$, million oz</th>
<th>Annual refined production$^c$, million oz</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3PGE$^d$ + Au</td>
<td>3PGE + Au</td>
<td>5PGE$^e$</td>
</tr>
<tr>
<td>Anglo Platinum</td>
<td>171</td>
<td>632$^f$</td>
<td>4.8</td>
</tr>
<tr>
<td>Implats</td>
<td>26$^g$</td>
<td>133$^g$</td>
<td>2.6</td>
</tr>
<tr>
<td>Lonmin</td>
<td>45</td>
<td>178</td>
<td>1.2</td>
</tr>
<tr>
<td>Northam Platinum</td>
<td>8</td>
<td>129</td>
<td>0.4</td>
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<tr>
<td>Totals</td>
<td>250</td>
<td>1072</td>
<td>9.0</td>
</tr>
</tbody>
</table>

$^a$These values are for the Bushveld Complex (i.e. they exclude Zimbabwe in all cases and toll refining in the case of Anglo Platinum and Implats). All data are taken from public sources published by the respective mining companies up to the end of calendar year 2009

$^b$Unless otherwise stated, resources are inclusive of reserves

$^c$Production data compiled by Alison Cowley, Principal Market Analyst, Johnson Matthey, August 2010

$^d$3PGE = Pt, Pd and Rh

$^e$5PGE = Pt, Pd, Rh, Ir and Ru

$^f$Resources quoted by Anglo Platinum are exclusive of reserves

$^g$Reserves and resources quoted by Implats are for platinum only

Probably nearly half that figure of 350 million oz has already been mined from the Bushveld Complex and most of it from depths of less than 1 km. So we can assume that there are around 200 million oz remaining in the upper one km, and 350 million ounces in the second km. Since mining in some cases is already at more than 2 km vertical depth (as at the Northam Platinum Mine), assuming material to that depth can all be mined is technically straightforward. Mining to greater depth will encounter high temperatures and serious rock stresses. However, mining of the Witwatersrand gold reefs has progressed to a depth of 4 km. Hence, mining of Bushveld reefs to comparable depths should not be considered implausible during this century.
The Platreef

In calculating a figure of 350 million oz platinum per km depth I have excluded the Platreef. Evaluating its total PGE content is more difficult. Evaluating the mineable PGE is even harder. The PGE mineralisation is distributed over vertical intervals that can reach 100 m in some borehole intersections, but more usually is intermittent over 50 m. Tracing the best mineralised horizons from one borehole to another is difficult – grade varies, thickness varies, and their location is not at a constant geological elevation. Best mining methods then also become an issue. Currently, all mining on the Platreef is by open pit methods, but it is limited to probably 500–800 m depth. Drilling has shown that the Platreef continues to at least 2 km depth. Methods of underground mining of this wide ore body are still being developed. As a result the estimates in Table I for the Platreef show considerable variation.

Other Chromitite Layers

Every chromite-rich layer of the Bushveld Complex contains some PGE. Very little systematic work has been done to evaluate these layers since the grade is in the range 1–3 g t\(^{-1}\) of PGE (10). The chromite ore itself is also currently sub-economic for chromium. The layer thickness and chromium-to-iron ratio are the two most important parameters in evaluating the economic potential of chromite deposits, and the chromite layers of the Bushveld Complex generally decrease in this ratio upward, and are in the range 2.0 to 1.2 (10). The layers with the highest values are too thin to mine. The thickest layers, which are mined, have ratios close to 1.6. Layers with a ratio of less than 1.4 are not economic at present. There is an inverse correlation between the PGE grade and the chromium-to-iron ratio in these layers. As with the PGE, there are extremely large proven reserves of chromium in the Bushveld Complex (1), even down to vertical depths of less than several hundred metres. Thus, if the chromium and PGE reefs that are currently being mined were ever exhausted one could mine the lower-grade chromitite layers for both chromium and PGE. Conservatively, we could suggest that these chromitite layers host nearly as much PGE and chromium as is presently considered potentially economic.

The tailings dumps from these chromite mines can be reprocessed to provide additional PGE. However they contain very minor PGE and, while some recovery is taking place, it will never represent a major additional supply.

Other Deposits of the Platinum Group Elements

The PGE contained in other deposits and exploration areas around the world tend to be much harder to define. They do not occur in such well-constrained layers of uniform thickness and great lateral extent. The mineralised layer in the Great Dyke of Zimbabwe is the most similar to the Merensky Reef, but the area of the intrusion is very much smaller. The Stillwater Complex in North America is also similar to the Bushveld Complex, but the ore zone is patchily concentrated along and vertically within a thicker layer than the Merensky Reef. The length of that entire intrusion is about 40 km, which is similar to that of one single mining operation in the

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**Example of the Calculation Principle for Estimate**

*Note 1:* This calculation is for platinum only, and also ignores the geological losses inherent in mining and process losses during refining (7).

*Note 2:* This calculation is purely illustrative of the basic simplicity of the concept behind such estimations of ore. All values have been rounded off for simplicity of multiplication and should not be taken quantitatively.

Combined strike length of outcrop in eastern and western Bushveld = 230 km = 230,000 m
Distance down the dip to 1 km vertical depth at an angle of 13º = 4.4 km = 4400 m
Mined thickness of Merensky Reef = 0.8 m, and of UG2 Reef = 0.8 m, combined thickness = 1.6 m
Density of Merensky Reef = 3.2 t m\(^{-3}\), density of UG2 Reef = 4.0 t m\(^{-3}\). Average of both reefs combined = 3.6 t m\(^{-3}\)
Grade of platinum only = 2 g t\(^{-1}\) = 0.06 oz t\(^{-1}\)
Weight of platinum only to 1 km depth = 230,000 × 4400 × 1.6 × 3.6 × 0.06 = 350 million oz
Rustenburg area (Anglo Platinum, Impala Platinum or Lonmin). The dip of the rocks in Stillwater is much greater, again reducing the ore tonnage to maximum mining depth.

The total potential of all the other PGE mining areas is much harder to quantify because they are not layered. Extensive exploration during the last ten years has failed to produce any new major targets or mines. Also, all occurrences in the Bushveld Complex and Great Dyke have high platinum-to-palladium proportions (platinum greater than palladium), whereas all other occurrences in the world are dominated by palladium.

Other Issues
Maintaining and increasing future production rates represent significant challenges. Resolving social, political and environmental issues, together with ensuring water and electrical supply capacities, needs ongoing monitoring and careful planning (11). These challenges are the unknowns and unpredictables in the future of platinum mining in South Africa, not the availability of the ores.

Conclusions
The estimates of the PGE presented here are not intended to be rigorous or quantitative. They are designed to show that the broad estimation of the PGE in the Bushveld Complex is extremely easy to make and to understand, and that the remarkably disproportionate concentration of the PGE in one geographic location, South Africa, is genuine. Even with current mining methods, technology and prices, there are many decades to a century of extractable PGE ore already known in the Bushveld Complex. With around 350 million oz of platinum per vertical km depth, the enormous deposits of PGE in the Bushveld Complex can be confidently relied upon to provide a major proportion of the demand needs for a long time into the future.

**Glossary**

<table>
<thead>
<tr>
<th>Term</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>3PGE</td>
<td>Platinum, palladium and rhodium</td>
</tr>
<tr>
<td>5PGE</td>
<td>Platinum, palladium, rhodium, iridium and ruthenium</td>
</tr>
<tr>
<td>anorthosite</td>
<td>A type of igneous rock largely composed of plagioclase feldspar, formed from intrusions of magma within the Earth’s crust</td>
</tr>
<tr>
<td>beneficiation</td>
<td>The processing of ore to produce minerals, also the further processing of minerals to metals and then to value-added products</td>
</tr>
<tr>
<td>Bushveld Complex</td>
<td>A large, layered, saucer-shaped geological formation found in the Bushveld region of the north of South Africa; it contains deposits rich in PGE</td>
</tr>
<tr>
<td>chromite</td>
<td>An iron chromium oxide (FeCr₂O₄) mineral with traces of magnesium and aluminium</td>
</tr>
<tr>
<td>chromitite</td>
<td>A rock type containing a high concentration of chromite</td>
</tr>
<tr>
<td>deflection</td>
<td>A secondary borehole drilled at an angle to the vertical</td>
</tr>
<tr>
<td>deposit</td>
<td>The total quantity of an ore body contained within a geological formation</td>
</tr>
<tr>
<td>dip</td>
<td>The angle of inclination of a reef from the horizontal</td>
</tr>
<tr>
<td>fault</td>
<td>A discontinuity in a layered feature resulting from rock fracture and movement, with one section being displaced relative to another</td>
</tr>
<tr>
<td>feldspar</td>
<td>An aluminium silicate mineral, containing potassium, sodium, calcium or barium</td>
</tr>
<tr>
<td>footwall</td>
<td>The layer of rock beneath a vein or expanse of ore</td>
</tr>
<tr>
<td>grade</td>
<td>The specific quantity of an element of interest contained within a unit mass of an ore body; for the PGEs this is most often given in grams per metric tonne</td>
</tr>
<tr>
<td>Great Dyke</td>
<td>A linear, layered geological feature running approximately north–south in the centre of Zimbabwe; it contains deposits rich in PGE</td>
</tr>
</tbody>
</table>
igneous Rocks formed from the solidification of either magma in the Earth’s crust or of lava on the surface

Merensky Reef A layer of the Bushveld Complex largely composed of pyroxenite that is rich in sulfide minerals; to date it has supplied most of the world’s platinum group metals, and also yields significant quantities of copper, nickel, cobalt and gold as byproducts. It is mined on both the eastern and western limbs of the Bushveld Complex

mineralised horizon A layer or stratum in which minerals of interest are preferentially concentrated; this could be distinct and continuous as a reef, or more dispersed and intermittent

outcrop A section of the reef which intersects the surface of the Earth and may have been subject to weathering

pegmatite A type of igneous rock characterised by a very coarse grain structure, with crystals several centimetres across usually composed of granite (quartz, feldspar and mica)

PGE Platinum group elements (platinum, palladium, rhodium, iridium, osmium and ruthenium). This term is used in geology as the elements generally occur in mineral, rather than metallic, form within an ore

plagioclase An aluminium silicate mineral of the feldspar family, with varying relative proportions of sodium and calcium

Platreef An ore body in the northern limb of the Bushveld Complex, it is the third largest PGE deposit in the world, after the Merensky and UG2 Reefs. It consists of three broadly mineralised horizons rather than a distinct reef

pothole Circular or elliptical sections where the reef has funnelled into the footwall, leading to discontinuity and altered mineralogy

pyroxene Silicate minerals containing calcium, magnesium and iron

pyroxenite A rock type containing a high concentration of pyroxenes

reef A distinct and continuous layer or stratum in which minerals of interest are preferentially concentrated

reserves Ore bodies which have been quantified to a high degree of confidence and which can be extracted using existing methods

resources Ore bodies which are known to exist and which can be quantified to some degree of confidence. These can reasonably be expected to be extracted in the future

sedimentary A type of rock formed from solidified deposits of eroded rock material, which have usually accumulated in bodies of water

strike The line of intersection of an inclined plane with the horizontal, such as when a reef outcrops on the surface of the Earth

sulfide Minerals formed from compounds of sulfur; these are a major source of metals such as copper, nickel and lead

tailings The waste material from ore processing, usually a slurry of finely ground rock in water, from which most of the valuable minerals have been removed

UG2 Reef Upper Group 2; a layer of the Bushveld Complex rich in chromite but lacking sulfide minerals. It possibly has a larger resource of platinum group elements than the Merensky Reef. It lies below the Merensky Reef and is mined on both the eastern and western limbs of the Bushveld Complex
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The Author

R. Grant Cawthorn is the Platinum Industry’s Professor of Igneous Petrology at the University of the Witwatersrand, South Africa. His main research interests are the genesis of the Bushveld Complex and its chromite, platinum and vanadiferous magnetite deposits, and the Insizwa intrusion and its copper and nickel deposits. His main fields of specialisation are the origin of mafic igneous intrusive rocks and their mineral deposits. He holds a BSc from the University of Durham, UK, a PhD from the University of Edinburgh, UK, and a DSc from the University of the Witwatersrand, South Africa.
Extraction and Refining of the Platinum Metals

A COMPLEX CYCLE OF SMELTING, ELECTROLYTIC AND CHEMICAL OPERATIONS

By A. F. S. Gouldsmith, A.R.S.M., B.Sc., and B. Wilson, B.Sc., F.R.I.C.

Platinum Refineries, Johnson Matthey & Co Limited

A major development in the world's platinum industry took place in the early nineteen twenties when large deposits of platinum bearing ore were discovered in the Transvaal in South Africa. This led to the formation in 1931 of Rustenburg Platinum Mines Limited to work these deposits, and this company remains to this day the only platinum producer in South Africa and the only major producer in the world whose prime activity is the extraction of the platinum metals.

From the outset Johnson Matthey has been associated with Rustenburg, first in developing methods for the extraction of the platinum metals from these ores, and thereafter as smelters and refiners of the output from the mines.

This article describes the complex and lengthy cycle of operations required to effect complete recovery of the six platinum metals and to yield at the same time electrolytically refined copper and nickel.

Today the joint activities of Rustenburg and Johnson Matthey constitute the world's largest source of the platinum metals in all forms. Together they ensure to industry throughout the world adequate and continuing supplies of these metals.

The earlier stages of the mining and recovery of the platinum metals from the Rustenburg Platinum Mines have been reviewed in some detail in this journal (1), while the geology of the Bushveld Igneous Complex and the platinum reefs—constituting an enormous reserve of platinum metals—which are mined by the Rustenburg company has also been described (2). This article deals with the succeeding stages of extraction and refining carried out in the smelting works and refineries of Johnson Matthey & Co Limited in order to bring the concentrates received from the mining company into marketable forms.

Operations conducted at the mine result in two products—a rich gravity concentrate which is passed directly to the wet process refinery of Johnson Matthey, and a converter matte that has been worked up from the flotation concentrate. This matte is cast and either prepared for shipment to the Johnson Matthey smelter at Brimsdown in the United Kingdom or sent to Matte Smelters (Pty.) Limited, a company formed in South Africa in 1952 as a joint subsidiary of Rustenburg Platinum Mines and Johnson Matthey in order to cope with the increasing output from the mines. The process operated at this plant, which is adjacent to the Rustenburg mine, is essentially the same as the primary stages of the Brimsdown process.

During the past thirty years the quantities of matte received at the Brimsdown refinery have increased, and in 1950 a new plant was
added, bringing the site for treating Rustenburg matte at Brimsdown up to a total area of ten acres.

Improved techniques and more modern equipment are always under review, but the basic process for extraction of the platinum metals has remained essentially the same.

Rustenburg converter matte contains about 46 per cent of nickel and 28 per cent copper, together with some other base metals and sulphur. The platinum group metals, together with some gold, total about fifty ounces to the ton. The complete process of extraction consists essentially of enriching this matte to approximately 65 per cent content of platinum metals and then treating this concentrate with acids to separate the individual platinum group metals from each other, followed by final refining.

Operations to achieve this can roughly be divided under three headings:

1. Smelting operations, where the original matte is broken down to yield metallic nickel and copper anodes.

2. Electro-refining operations, where these anodes are dissolved electrolytically to produce pure nickel and copper and anode slime containing the precious metals.

3. Chemical operations, for the separation and refining of the individual metals.

**Smelting Operations**

Converter matte from Rustenburg arrives at the Brimsdown smelter in bags of about 150 pounds each. It has been crushed to three-inch size. After weighing and sampling the first operation is to separate the nickel and copper sulphides. This is done by making use of the fact that molten sodium sulphide is completely miscible with copper sulphide and completely immiscible with nickel sulphide, so that if the converter matte is melted with sodium sulphide two fractions separate out—a sodium sulphide/copper sulphide layer floating on a nickel sulphide layer. Furthermore, a nickel matte with a deficiency of sulphur is an excellent collector of the platinum group metals; therefore under suitable conditions a nickel matte can be produced that is low in copper and will contain the platinum group metals. At Brimsdown this operation is mainly carried out in a blast furnace, although six-ton
The first stage of the smelting operations is a blast furnace treatment to separate nickel matte containing very small amounts of copper and practically all of the platinum metals.

The copper tops are then either poured into a five-ton reverberatory holding furnace or directly into a horizontal-type copper converter. The converter is lined with magnesite brick and capable of taking charges up to five tons. By blowing air through the molten top considerable heat is generated and sodium sulphate is first formed. This is tapped off as a watery liquid and used again in the blast furnace. Silica is then added to the converter to flux iron oxide and any excess soda; this slag is also poured off and the residual copper sulphide blown down to blister copper in the normal way. The blister copper is tapped into a ladle and poured directly into one of three small reverberatory furnaces. The copper is then further refined and cast into moulds.

Reverberatory furnaces are also used. The blast furnace is water-jacketed for its full height and has a rectangular hearth measuring 72 x 36 inches. Converter matte, salt cake (sodium sulphate) and coke are fed in and the molten materials run into a settler where the sodium sulphide/copper sulphide top layer flows continuously into a ladle, while the bottom layer of nickel matte is tapped intermittently. By careful control of temperature and sulphur content a nickel matte can be obtained containing little copper and all the platinum metals, whereas any gold will have followed the copper sulphide into the "tops" layer.

Casting the enriched nickel matte into pigs. These are then crushed, ground and roasted.

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to make anodes for the electro-refinery.
In the meantime, nickel matte from the blast furnace operation is broken, crushed and ground in ball mills to 20 mesh. This material is then roasted to nickel oxide in oil-fired 17-feet diameter Herreshoff type furnaces with two hearths separated by an air gap. Ground nickel matte is fed through a hopper on to the top hearth which is kept at a low temperature; it then falls through to the lower hearth which is kept at 900 to 950°C. After cooling, the resultant nickel oxide is briquetted with anthracite coal and sand. These briquettes are next charged into an oil-fired reverberatory type furnace, where the oxide is reduced to metal and tapped into anode moulds. These anodes, which contain practically all the platinum metals, are then passed into the electrolytic nickel refinery.

Electro-Refining Operations
Copper anodes from the converter process are dissolved electrolytically using an acid copper sulphate solution as an electrolyte. The products of this operation are pure copper cathodes and an anode slime which may contain gold and small quantities of the platinum group metals.
The cells are constructed of rubber-lined concrete. Internal measurements are approximately $8\frac{1}{2} \times 2 \times 3$ feet. The warmed electrolyte is fed in at one end and overflows from the other into a launder running between the lines of cells. From the launder the liquid is pumped to overhead tanks where its heat is maintained, and by gravity flows to a manifold which feeds it back to the cells. During electrolysis the electrolyte tends to accumulate nickel and quantities have to be bled off occasionally and replaced by pure copper sulphate. The impure electrolyte is treated for recovery of the copper sulphate and the nickel sulphate is passed to the nickel refinery. There are 21 anodes and 20 cathodes in each cell and a current of $15\frac{1}{2}$ amp per square foot is maintained. The quantity of anode slime formed by the dissolving of these anodes is small and falls to the bottom of the cells, where it is periodically recovered.
The dissolving of the nickel anodes follows the same general pattern, the products...
The electrolytic nickel refinery at Birmsham. Here pure nickel cathodes are produced, while the platinum metals accumulate in the anode residues and are removed for the separation and refining of the individual metals.

being pure nickel cathodes and an anode slime containing the bulk of the platinum group metals. In this case the electrolyte is a neutral solution of nickel sulphate containing boric acid as a buffer and has to be continually purified to produce a pure cathode. Copper and iron are present in the anodes and being more electro-negative than nickel must be removed from the electrolyte or they will deposit on the cathode as impurities. To achieve this each cathode is placed in a calico bag with purified electrolyte flowing into it, so that the cathode will grow in clean liquor. The stripped liquor flows out of the bag laterally and picks up the impurities from the solution of the anode. This liquor flows out of each cell into a launder and is pumped across to large circular treatment tanks where it is heated to approximately 70°C. An emulsion of nickel carbonate is added to adjust the pH and air is blown through to hydrolyse out the iron. After this any copper present is precipitated and the contents pumped through a filter press to separate out the solid impurities.

The filtered liquor is stored in overhead tanks ready for feeding back to the cells.

As in the copper refinery, the cells are constructed of rubber-lined concrete and 24 cells make up one unit. Internal dimensions of the cells are about 11¾ x 2 x 2¾ feet. There are 21 anodes and 20 cathodes in each cell and the current density is 12½ amp per square foot. Anodes and cathodes in each cell are in parallel.

The quantity of slime produced by the nickel anodes is far greater than from the copper anodes and although a little falls to the bottom of the cells the majority adheres to the anode and has to be scraped off. This is normally done every 100 running hours, both to bring the platinum metals forward and to stop the anodes becoming passive.

During all the processes that have been described so far slag, residues and flue dust have been produced. Normally these are worked into a previous stage of the process, but in primary work several products result which although poor in values compared with the initial matte are far too valuable to be
thrown away. These are collected, blended with suitable fluxes and smelted in a blast furnace to a matte which is blended in with the original matte at the beginning of the process.

**Chemical Operations**

From this stage onwards the concentration of the platinum group metals is more rapid and the processes entirely chemical. First the slime is subjected to roasting and leaching attacks to remove the last of the copper, nickel, iron and sulphur. This produces an enriched slime running approximately 65 per cent of the platinum group metals and gold.

At this point the platinum-bearing gravity concentrates shipped from South Africa join those produced in the Johnson Matthey smelting plant, and together enter the wet process refinery. Here they are treated for complete elimination of base metals, and the platinum metals are brought into solution for their separation and individual refining. The solutions handled are usually highly concentrated, extremely valuable and very corrosive. Handling is therefore carried out by employing the simplest possible methods, including siphoning and gravity draining, and use is made of glass-lined vessels, glass pipelines and glandless pumps of chemically resistant materials.

The complete cycle of treatment is very complex and can only be briefly outlined here. Basically the separation and refining of these six closely allied metals involves their precipitation as complex salts followed by successive stages of recrystallisation and then by calcination, under carefully controlled conditions in electrically heated muffle furnaces, to produce the metals in the form of sponges or powders suitable for melting and working.

Initial treatment comprises digesting with aqua regia to produce a solution containing the major portion of the gold, platinum and palladium as chlorides, the residue comprising the more insoluble metals, iridium, rhodium, ruthenium and osmium. The solution is reduced by adding ferrous chloride to remove the gold. The addition of ammonium chloride to the filtrate precipitates impure ammonium chloroplatisate, which is calcined to a crude platinum sponge, redissolved, reprecipitated

*The initial step in the wet process refinery comprises digestion with aqua regia to dissolve the platinum and palladium, leaving the other four metals as an insoluble residue*
This section of the wet process refinery – the largest of its kind in the world – handles the precipitation, redissolving and reprecipitation of platinum and palladium. It is arranged on the cascade system to facilitate the movement of solutions as pure ammonium chloroplatinate and calcined again to give pure platinum sponge. The filtrate from the ammonium chloroplatinate is oxidised, and excess of ammonium chloride added to precipitate the palladium as a crude ammonium salt. This is redissolved in ammonia to form a tetrammino palladium chloride, which on acidification precipitates palladium diammino dichloride. This salt is then calcined to pure palladium sponge.

The other four metals are extracted from the original insoluble residue, first by fusion with alkaline and oxidising fluxes, followed by dissolution in water and then by distillation.

In this part of the refinery the four “insoluble” metals – ruthenium, rhodium, iridium and osmium – are extracted and separated as their complex ammonium salts.
of ruthenium and osmium as volatile oxides. These distillates are then treated in a similar way to the solutions of the soluble metals, by precipitation of their complex salts and calcination to metal.

The solution remaining after distillation contains the iridium and rhodium, which are recovered as sodium salts, followed again by precipitation of their complex ammonium compounds and calcination.

The whole of the plant, the largest of its kind in the world, is arranged on the cascade system, so that all movement of liquids is by gravity. The methods employed achieve an extremely high degree of purity in each of the metals. For example, routine production of platinum yields a metal of 99.99 per cent purity, while additional steps in refining metal required for special purposes give a product totalling only a few parts per million of impurities.

In every case the metals produced are subjected to chemical and spectrographic analysis. After meeting the specified requirements, the sponges are converted to solid metal—or to alloys—either by melting in high frequency induction furnaces or by the method of powder metallurgy, followed by forging and rolling.

From this refinery the six platinum metals are supplied in pure form to independent fabricators and users throughout the world, to Johnson Matthey associated companies in the United States, Canada, South Africa, Australia, Belgium and Italy, and to the company's London manufacturing centre.

References

"The Story of Platinum"

Produced by N. de Klerk, sponsored by TWP Holdings Ltd and distributed by The South African Institute of Mining and Metallurgy, PO Box 61127, Marshalltown, Johannesburg, 2107, South Africa, September 2009, DVD, Runtime: 85 mins (approx.), 2 discs, R100


Reviewed by M. Ryan
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A new DVD documentary, “The Story of Platinum”, has been produced in South Africa by Neels de Klerk, an independent video producer with experience in the South African gold, coal and platinum mining industries. The documentary grew from de Klerk’s interest in the subject, and his desire to illustrate to workers in the platinum industry how their contribution fits into the bigger picture (1). To paint this picture in full required the collaboration of many international companies, including Anglo Platinum in South Africa and Johnson Matthey in the UK. The production of the DVD was sponsored by TWP Holdings, a company which provides engineering and consulting services to the mining industry. All proceeds from its sale will go to the South African Institute of Mining and Metallurgy (SAIMM) Scholarship Trust Fund, a charity which aims to promote careers in the minerals industry and supports deserving students in relevant disciplines who are in need of financial assistance (2).

The DVD is presented in two parts, each of approximately 45 minutes’ duration. The first part summarises the history of platinum, from the first recorded encounters in the 16th century to the discovery of platinum in the Bushveld Complex in the early 20th century, and finally the establishment of full refining facilities in South Africa. The second part of the documentary deals in more detail with the processes involved in extracting platinum from its ore, and also briefly discusses the metal’s many applications.

The Discovery of a New Metal

The historical part of the story of platinum is illustrated in the DVD documentary using photographic stills and drawings, and is told in such a way that interest never flags.

It provides an overview of modern man’s association with platinum, from the first discovery of an unworkable silvery metal contaminating South American gold mines in 1557, to the naming of platinum as a separate element in 1777 and its first successful melting in 1782. This scientific progression is echoed by the commercial exploitation of the new metal: initially used only to adulterate gold in the 16th
and 17th centuries, it gained increasing status and was considered a decorative and desirable metal in its own right by the time of Louis XVI of France.

The discovery of geological deposits of platinum is traced from the metal’s first occurrences as a byproduct in gold or nickel mines in Russia and the Americas, to the eventual discovery in the 1920s of a primary platinum deposit in the abundant reserves of the Bushveld Complex in South Africa (Figure 1). The detail behind the exploitation of these reserves is vividly recounted, as are the many ups and downs in the course of the metal to its current position of economic significance.

The decorative uses for the metal were not what ultimately drove growth in demand for platinum. The documentary recounts how, in the early days of platinum mining in South Africa, supply had to be controlled to avoid flooding the market. After the Second World War, when the price of platinum suddenly escalated due to its use as a catalyst in the production of gasoline, it became clear that much of the value of the metal lay in its great industrial utility. As many new applications for platinum were discovered, demand rapidly increased and production expanded to keep pace. South Africa became the world’s leading supplier of platinum, and today accounts for around 80% of annual global platinum production.

The Processing of Platinum

The second part of the documentary is an overview of the complex process that turns platinum ore into platinum metal. Even from the fertile Merensky Reef of the Bushveld Complex about ten tonnes of rock are need-

![Fig. 1. Panning for platinum in the eastern Bushveld in South Africa in 1924. Dr Hans Merensky (centre), after whom the Merensky Reef is named, looks on (3)](image)

![Fig. 2. The concentrate product obtained from froth flotation. After the ore is mined, it is crushed, mixed with water and milled down to a fine size to liberate the valuable minerals from the host rock. Once these minerals are free, their natural hydrophobicity is enhanced to allow the particles to adhere to the surface of air bubbles, which rise to the surface and leave behind most of the unwanted material. This is only one of many processes that must be carried out to produce platinum metal, all of which are discussed in the documentary)](image)

ed to obtain a single ounce of platinum. How the ore is extracted from the earth and subsequently treated to yield its metal content (Figure 2) is described in some detail in the DVD, which will doubtless be of considerable value as an educational tool in mining and metallurgy.

Concluding Remarks

For anybody wishing to gain insight into the history and production of platinum, this documentary is very informative and provides an excellent overview. The DVD costs R100 plus postage and there is also a commemorative montage poster which costs R150; these can be obtained from the SAIMM in South Africa, by contacting Julie Dixon by E-mail at julie@saimm.co.za, or phoning +27 11 834 1273 (2).

References

CATSA 2009 Conference

An update in heterogeneous catalysis from the Catalysis Society of South Africa

Reviewed by Jason McPherson
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The Catalysis Society of South Africa (CATSA) is an organisation that aims to promote the advancement of catalysis amongst academia and the chemical industry in South Africa (1). The history of CATSA dates back to the late 1970s, when Dr Wim Mandersloot from the Council for Scientific and Industrial Research (CSIR) began organising annual meetings for catalysis researchers in South Africa. From a handful of people, the attendance at these annual conferences had grown substantially, and as a result CATSA was founded in 1990. Catalyst research in South Africa is ‘alive and well’ with the following programmes playing a substantial part in growing the field:

- **c*change**™ (the South African Department of Science and Technology – National Research Foundation (DST-NRF) Centre of Excellence in Catalysis)
- HySA (Hydrogen South Africa, the DST’s National Hydrogen and Fuel Cell Technologies Research, Development and Innovation Strategy)
- Project AuTEK (an Anglogold Ashanti, Goldfields, Harmony Gold and Mintek sponsored project to find industrial uses for gold).

There has also been much ‘contracted’ and public research funded by South African companies such as Sasol and PetroSA.

The latest annual CATSA conference, CATSA 2009, took place at the Goudini Spa outside Cape Town, South Africa, from 8th–11th November 2009. The meeting was sponsored by BASF, PetroSA, Poretech (local Micromeritics agent), Sasol and Süd-Chemie. Stellenbosch University hosted the event, which was attended by approximately 250 delegates from both academic and industrial backgrounds. All thirty oral presentations were conducted in a single session spread over three days, and there was a single poster session comprising 103 posters.

As well as good coverage of South African research, there was a strong international flavour at this conference with nine of the thirty oral presentations given by non-South African based speakers. In addition, the CATSA Eminent Visitor Award, which aims to bring international researchers to South Africa, was bestowed on Professor Bert Weckhuysen (Utrecht

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University, The Netherlands). His Plenary Lecture focused on in situ spectroscopy of heterogeneous molybdenum-, iron- and cobalt-based catalysts as well as zeolites.

The scientific programme focused on the main interests of the local community, namely heterogeneous catalysis, homogeneous catalysis and biocatalysis.

Given Sasol’s prominent position in South Africa’s petrochemical industry, it was unsurprising that the majority of oral presentations and posters in the area of heterogeneous catalysis were devoted to the Fischer-Tropsch process and associated issues regarding feed and product clean-up. There were however a few oral presentations on environmental catalysis. This selective review describes some of the highlights relevant to the platinum group metals (pgms) as well as gold.

**Carbon Monoxide Oxidation**

The major issues regarding the use of supported gold nanoparticle catalysts for CO oxidation are catalyst deactivation and precious metal cost. Furthermore, it is well known that these nanoparticles are difficult to characterise by standard techniques. Dean Barret, Mike Scurrell and Paul Franklyn (University of the Witwatersrand, Johannesburg, South Africa) reported on efforts to prevent the sintering of gold nanoparticles on silica and titania by the addition of platinum. A series of supported gold-platinum bimetallic catalysts of varying precious metal ratios were synthesised and characterised by powder X-ray diffraction (PXRD), in situ variable-temperature powder X-ray diffraction (VT-PXRD) and high-resolution transmission electron microscopy (HRTEM). Results showed that the addition of platinum stabilised the gold nanoparticles, and thus the bimetallic gold-platinum nanoparticles are more resistant to high temperatures than monometallic gold nanoparticles. This bodes well for the application of such materials at high temperature (100–600°C).

The thrifting of precious metal from gold catalysts using cyanide leaching was explored by Mike Scurrel (University of the Witwatersrand, Johannesburg, South Africa) reported on efforts to prevent the sintering of gold nanoparticles on silica and titania by the addition of platinum. A series of supported gold-platinum bimetallic catalysts of varying precious metal ratios were synthesised and characterised by powder X-ray diffraction (PXRD), in situ variable-temperature powder X-ray diffraction (VT-PXRD) and high-resolution transmission electron microscopy (HRTEM). Results showed that the addition of platinum stabilised the gold nanoparticles, and thus the bimetallic gold-platinum nanoparticles are more resistant to high temperatures than monometallic gold nanoparticles. This bodes well for the application of such materials at high temperature (100–600°C).

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Deactivation and Commercial Issues

The issues of catalyst deactivation and regeneration were highlighted by Robert Parry (BASF Catalysts, Haslemere, Surrey, UK) including:

- **Poisoning**: e.g. poisoning of Pt hydrogenation catalysts by species such as sulfur, selenium, tellurium, phosphorus, arsenic, zinc, mercury, lead, halides, ammonia and ethene; and poisoning of Pt/Pd automotive catalysts (for oxidation of CO and hydrocarbons) by lead, phosphorus and zinc.

- **Thermal degradation**: e.g. for Ni/Al₂O₃ catalysts which transform to non-catalytic nickel aluminate at high temperature, the addition of Rh or Ru enhances catalyst stability. Furthermore, sintering of a base metal catalyst may be prevented by the addition of a higher melting point noble metal (e.g. Rh or Ru).

- **Escape of vapours**: e.g. Ru may be lost from a catalyst on exposure to air at room temperature through the formation of ruthenium trioxide which is then converted to volatile ruthenium tetroxide.

- **Regeneration**: e.g. a sintered reforming catalyst (such as Pt/Al₂O₃) may be regenerated by oxychlorination which involves exposure to a chlorinating agent mixed with 5% O₂ in N₂ at 450–500°C for 1–4 hours. This results in the formation of AlCl₃ and thereafter of PtCl₂(AlCl₃)₂ which can be reduced to form monodispersed Pt clusters. The AlCl₃ is transformed back into Al₂O₃ during this process.

Geoffrey White (BASF Catalysts, Beachwood, Ohio, USA) discussed the turnaround of industrial catalytic reactors. He described the special loading and activation procedures required by eggshell-type pgm catalysts, and the subsequent recycling of the spent catalyst.

Environmental Catalysis

James Luiz Aluha, Gary Patrick and Elma van der Lingen (Mintek, Randburg, South Africa) presented a comparative study on the performance of Ni-Pd-Pt, Au-Pd-Pt and Au-Ni-Pd (supported on Al₂O₃ or TiO₂) as potential sulfur-tolerant diesel oxidation catalysts that would operate under a cold start engine regime. The addition of nickel was found to inhibit sintering...
of the precious metal, while in most cases deactivation was a result of poor alloy formation and the oxidation of Pd to PdO. It was found that Ni-Pd-Pt and Au-Ni-Pd performed better than Au-Pd-Pt for both low-temperature CO oxidation and total hydrocarbon oxidation (propane) below 350°C, even after ageing in SO2 at 500°C for 24 hours (see Figure 1).

**Chemical Synthesis**

In an effort to explain the promotional effect of potassium on the rate of ammonia synthesis from H2 and N2 over ruthenium and rhodium catalysts supported on active carbon, Sanyasi Sitha and Linda J. Jewell (University of the Witwatersrand) carried out a density functional theory study in which the adsorption of nitrogen on Ru10 and Rh10 (neutral and anionic clusters, in order to account for the effect of promoter electron density) was presented. Ru catalysts are known to be active for ammonia synthesis, while Rh catalysts require potassium promotion to generate activity. In each case three types of interactions (super molecules) were identified (see Figure 2) with Ru showing only one super molecule as stable when neutral or anionic (potassium promoted). By contrast the neutral Rh cluster shows all three super molecules as stable, while an anionic Rh cluster only has one stable super molecule.

The synthesis of gold-polyaniline composite catalysts by the addition of HAuCl4 to polyaniline, followed by reduction with sodium borohydride, was reported by Tlhabologo Kabomo and Mike Scurrell (University of the Witwatersrand). Characterisation of this material by transmission electron microscopy (TEM) showed a mean gold particle size of 3.2 ± 0.8 nm, and X-ray photoelectron spectroscopy (XPS) revealed that the majority of the gold is on the polyaniline surface in a metallic state. Shifts to low-energy operation revealed that gold interacts with the nitrogen atom of the polyaniline. Gold nanoparticle size was also found to decrease with increasing ratios of sodium borohydride to gold. The pH during synthesis was also found to affect gold particle size, with particles less than 5 nm in diameter being formed at pH values above 3. This was explained by the fact that polyaniline becomes protonated at pH values below 3, and is deprotonated at higher pH values. A test reaction using a gold-polyaniline composite catalyst for the reduction of 4-nitrophenol to...
4-aminophenol was performed, and this demonstrated that the rate of reaction increases with decreasing gold particle size.

**Poster Presentations**

The most interesting of the posters involving precious metals are summarised below:

‘**High Dispersion Platinum Catalysts on Mesoporous Carbon Support for Fuel Cells**’ by Hanna S. Abbo, Ivan R. Green and Salam J. J. Titinchi (University of the Western Cape) reported the development of a polyl process capable of generating well-dispersed 1–3 nm Pt nanoparticles deposited on different types of carbon supports for use as electrocatalysts for oxygen reduction in fuel cells. This method is claimed to have many advantages over others in that it gives high yield at low cost and is environmentally benign.

‘**Gold Catalysed Glucose Oxidation Techno-Economic Assessment**’ by Brendan Beeming and Gary Pattrick (Mintek, Randburg, South Africa) described a gold-catalysed glucose oxidation process which allows the more economic production of gluconic acid and sodium gluconate than the current enzymatic technology. 190,000 tons of gluconic acid and its salts are produced annually, with the main product being sodium gluconate for use as a cement setting retardant in the construction industry. The gold-catalysed process therefore offers producers with smaller plants an opportunity to compete in this aggressive market where economies of scale dominate in terms of the enzymatic process.

‘**Platinum Nanowires Supported on Surface-Decorated Carbon Sphere and Their Electrochemical Performance**’ by Feng Li, Gary Pattrick and Elma van der Lingen (Mintek, Randburg) reported that Pt nanowires can be grown on Vulcan XC72R via the formic acid reduction method by employing a nitric acid pretreatment of the carbon. Results indicated that the surface pretreatment process introduces large amounts of oxygenated groups (such as carboxylic and hydroxyl), and high-resolution scanning electron microscopy (HRSEM) showed that these oxygenated groups favour the growth of Pt nanowires. Electrochemical characterisation showed higher oxygen reduction reaction (ORR) activity for Pt nanowires grown on surface-decorated carbon spheres when compared to nanowires on raw carbon black.

‘**Microwave Polyol Synthesis of Ru/CNT Catalysts**’ by L. F. Mabena, R. Suprakas and N. Coville (School of Chemistry University of the Witwatersrand) presented a simple method to prepare Ru nanoparticles on carbon nanotubes using sodium citrate stabiliser and ethylene glycol as a reducing agent to reduce RuCl₃ by microwave irradiation. The intention here was to prepare a material suitable for alkaline fuel cells.

‘**Oxygen Chemisorption on Alumina Supported Gold Catalysts**’ by Jennifer Case, Eric van Steen and David W. Gammon (Department of Chemical Engineering, University of Cape Town) discussed the use of oxygen chemisorption to determine the metal crystallite size for Au/Al₂O₃ catalysts. Unlike pgm catalysts, gold catalysts cannot be characterised using H₂ or CO adsorption, since they tend to oxidise these gas species at very low temperatures. By measuring oxygen uptake at 200°C over a pressure range of 0.1–700 mm Hg and using a dual isotherm model, the spherical crystallite sizes can be calculated. These calculated values were found to agree with those arrived at by TEM.

‘**Formation of Supported Rhodium Nano Crystallites of Controlled Size and Their Application in CO Hydrogenation**’ by Nothando Mungwe, Eric van Steen and Michael Claeys (Department of Chemical Engineering, University of Cape Town) described a method of preparing model catalysts with varied Rh crystallite sizes (2–14 nm) using a novel reverse micelle method.

‘**Hydrogen Spillover in the Fischer-Tropsch Synthesis: the Role of Platinum and Gold as Promoters in Cobalt-Based Catalysts**’ by Doreen Nabaho, Eric van Steen and Michael Claeys (Department of Chemical Engineering, University of Cape Town) demonstrated that gold is a likely candidate as a promoter for low-temperature Fischer-Tropsch catalysts, given that platinum is more expensive and also results in increased methane selectivity which lowers the yield of desired higher hydrocarbons. Initial results show that gold, just like platinum, also increases the reducibility of cobalt oxides. It remains to be seen if the gold promoter will result in a lower affinity for carbon monoxide making it less ‘methanating’ than a platinum promoter.

**Conclusions**

South Africa is the leading source of pgms and there is a need for local beneficiation and to add value to this commodity within South Africa. Novel catalyst research offers a possibility in this regard, and with the establishment of HySA, c*change™ and other support initiatives South African pgm research will continue to grow in areas such as the hydrogen...
economy (fuel cells, hydrogen storage etc.) and emissions control, and as promoters for base metal catalysts (e.g. cobalt-based low-temperature Fischer Tropsch catalysts).

The abstracts of the oral and poster presentations given at this conference are available by emailing the CATSA Media Officer, Cathrin Welker, at: cathrin.welker-nieuwoudt@sasol.com. The next meeting (CATSA 2010) is planned to be held from 7th–10th November 2010 on the Campus of the University of the Free State in Bloemfontein, South Africa (2).

References


The Reviewer

Jason McPherson completed his postgraduate studies in precious metal catalysis at the University of Cape Town, South Africa, in 2003. Currently he heads up the Scale-up and Commercialisation Unit of Project AuTEK’s Catalysis Programme (Mintek, South Africa) and as such is actively involved in the production, marketing and application of AuTEK’s AUROlite® range of gold catalysts. He is highly active in application areas such as CO oxidation, preferential oxidation, liquid phase oxidations (e.g. glucose, glycerol) and selective hydrogenation. He is also a technology advisor to the World Gold Council (London, UK) and is currently the Chairman of the Catalyst Society of South Africa.
Carbon nanotubes (CNTs) possess unique properties which make them competitive with conventional catalyst supports. This short review collates findings from many research groups on the benefits of palladium/carbon nanotubes in hydrogenation reactions. The effects of modified CNTs and bimetallic platinum group metal (PGM) catalyst/CNT systems for hydrogenation reactions are also discussed.

Introduction

The need to optimise industrially important processes and new technologies, and to create a sustainable society and environment, drives the search for better energy sources and better materials. Coupled with this is the need for economic development and competitiveness in the global market. Worldwide trends are towards greener chemistry, greener energy and a decrease in our reliance on fossil fuels. Catalysis plays an important role in this and two recent papers have discussed how it has shaped, and will continue to shape, society (1, 2). Progressive research into novel catalytic systems is a part of this endeavour.

Palladium is one of the most versatile metal catalysts used in industry. Two of the main reasons for its importance are its ability to catalyse the formation of carbon–carbon bonds and the insensitivity of many Pd catalysts to water or oxygen. Pd is particularly efficient as a catalyst in hydrogenation reactions. Metal catalysts reach a much greater potential when supported. This is because metal catalyst particles can be dispersed to a greater degree, and therefore are exposed to a larger number of substrate molecules. Up to 75% of hydrogenation reactions are currently carried out over Pd/C catalysts.

A variety of carbon supports for precious metal catalysts have, for several decades, been used in heterogeneous catalysis (3). Emerging carbonaceous supports, such as the newly discovered carbon allotropes and shaped carbon nanomaterials (SCNMs), including CNTs (4), see Figure 1(a), carbon microspheres (5),
see Figure 1(b), and carbon nanofibres (CNFs) (6), see Figure 1(c), are gaining more interest. The remarkable properties of CNTs, such as being relatively light in weight and strong in nature, make them worthwhile to investigate as supports for Pd metal catalysts. Although the existence of filamentous carbon nanomaterials (7) has been known for decades, it is only since the report in 1991 by Iijima (8) that many researchers have devoted much time and effort in developing new strategies for the synthesis of SCNMs.

Trends in technological and scientific progress in catalysis lean towards the production of more efficient catalysts, smaller particle sizes and more finely dispersed particles to optimise yields and decrease reaction times. For this reason, nanosized catalytic particles have received much attention and they are known to display higher catalytic activity (9). Hybrid metal-CNT systems have been shown by theoretical calculations to have altered properties compared to unmodified CNTs (10). The results of hydrogenation reactions on various supports suggest that the interaction between the metal catalyst and the support greatly influences the catalytic activity in a hydrogenation reaction (11–13). Hence, this review addresses the issue of catalyst support use with the aim of broadly answering the following questions:

- How do CNTs compare with other traditional carbonaceous supports for catalysts and in what cases are CNTs superior as Pd supports in hydrogenation reactions?
- How do chemically modified CNTs influence the activity of Pd nanoparticles (NPs), especially in hydrogenation reactions?
- What effect does a secondary metal have on the catalytic activity of the Pd/CNT system?

Lastly, we look at a few literature examples involving the use of Pd/CNT hybrids in hydrogenation reactions.

This article covers a wide range of literature on Pd/CNT systems. The examples chosen for this review mainly involve some current studies of Pd/CNT systems for hydrogenation reactions. Specifically, examples based on cinnamaldehyde (Figure 2(a)), which has useful applications such as a flavouring, fungicide, antimicrobial agent or anticancer agent among others, are provided. The reduction of this organic compound is interesting because it has more than one functional group that can be reduced. The useful products that are obtained include cinnamyl alcohol (Figure 2(b)), 3-phenylpropanaldehde (Figure 2(c)) and 3-phenylpropan-1-ol (Figure 2(d)), among others, depending on chemoselectivity. Hence, this compound, as an example, could form the basis for the comparison of conversions and the effect or influence of the support on Pd chemoselectivity.

Synthesis of Carbon Nanotubes

CNTs and other SCNMs can be made by a variety of procedures and these include numerous variations of arc discharge (14, 15), laser ablation (16, 17) and chemical vapour deposition (CVD) processes (18–21). In the arc discharge and laser ablation methods, the catalysts required for synthesis are generally made from metals or metal salts. Both of these methods produce relatively pure CNTs but are currently not easy to scale up to industrial levels of production. The CVD processes, by contrast, allow for easy scale-up.

There are two main approaches to the CVD synthesis of CNTs. The first method entails passing a gas phase carbon source over a supported catalyst. The catalyst used can be derived from any metal source including an organometallic complex (22). In the second method, both the catalyst and the carbon source are in the gas phase and the CNTs are formed in the
gas phase. This latter process is called the ‘floating catalyst’ method and typically requires volatile organometallic complexes.

Many studies have attempted to rationalise the mechanism of catalytic synthesis of CNTs. There is now a consensus as to the mechanism involved in the synthesis of CNTs over supported catalysts (23–27). In this process, small catalyst (metal) particles are deposited on a support and the carbon from the gas phase deposits onto, or dissolves in, the catalyst particle. For metals like iron and cobalt, growth of the CNT then arises from the precipitation of the carbon out of the metal. If the catalyst–support interaction is strong then the carbon tubes grow away from the support surface (‘base-growth’ mechanism), but if the catalyst–support interaction is weak, then the metal particle is displaced from the surface by the carbon (‘tip-growth’ mechanism) (27). The mechanism has been further simplified by Moisala et al., who proposed that the metal catalyst particles act as nuclei for the growth of CNTs in the gas phase (28).

Another type of CVD approach to CNT synthesis involves the reactions taking place in a closed container (for example, an autoclave or a sealed quartz tube) at elevated temperatures. Typically, in this method, organometallic complexes (at times containing an external carbon source) are used as starting materials (29–39).

**Catalytic Applications of Carbon Nanotubes**

CNTs exhibit extraordinary properties which are required for several potential applications (40). Among these applications, the use of CNTs as catalyst supports seems to be one of the most promising fields, with large economic implications. CNTs can be used as synthesised (‘pristine’) or can be modified, functionalised, doped or used as a part of a composite. Many applications involve hybrids or composites of CNTs with precious metal NPs. It is predicted that such composites will find uses in modern materials as well as industrial hydrogenation catalysts for liquid (41–43) and gas (44) phase processes.

**The Advantages of Carbon Nanotubes as Catalyst Supports**

A host of supports for Pd catalysts are available, from metal oxide supports such as alumina, silica and zeolites, to the traditional carbonaceous supports such as activated charcoal or activated carbon (AC), carbon blacks, graphites and the emerging carbon nanomaterials (3).

Oxide supports are often mechanically and thermally unstable. In the case of alumina, at high temperatures the ions of the catalytically active phase can interact with the support in such a manner as to lower the catalyst availability and catalytic activity (45). In transition aluminas, conversion to \(\alpha\)-alumina at temperatures near 1100ºC can occur, resulting in a lowered surface area (46). Heat dispersion in certain oxide supports, such as alumina, is not always uniform, due to the insulating nature of this material. Thus, under oxidising conditions, so called ‘hot-spots’ can form, resulting in alteration of both the support and catalyst metal (47).

There are a variety of AC products that differ in certain key properties such as porosity, pore size and particle size distribution, surface area, resistance to attrition and content of ash, depending on the process of manufacture. AC is commonly used in liquid phase processes and remains the popular choice of support for hydrogenation reactions. This is due to its ease of separation from the reaction mixture, resistance towards aggressive media such as high pH, and the relative ease of metal recovery after use. Carbon black, which is produced from acetylene under high temperatures, is more suitable for use as a support than conventional carbon black made from other petroleum fractions. However, carbon black in general has a relatively low ash content (3).

In order to overcome some of the disadvantages of the common commercial supports, there is a need to
research and develop new nanodimensional supports such as CNTs or CNFs. These nanostructured carbon-based materials display good physical and chemical properties which are ideal for catalyst supports. The two main types of CNT considered here are the single-walled carbon nanotube (SWCNT) and the multiwalled carbon nanotube (MWCNT) (Figure 3).

Electronic Properties
The arrangement of carbon atoms determines the surface and electronic properties of CNTs. According to theoretical predictions, the geometry of the ring structures imparts either a metallic or semi-metallic nature to CNTs (48, 49). This naturally has an effect on the properties of metals loaded onto the support. Duca et al. studied the combined properties of graphite versus SWCNTs with Pd₉ clusters by means of computational methods (50). Their findings showed that Pd₉ clusters may have a stronger interaction with a CNT than with traditional flat graphite sheet bilayers due to the curvature of the nanotube which has an effect on metallic properties.

Mechanical Strength
The high mechanical strength of CNTs makes them not only favourable in composites (47, 48), but also in mechanically taxing catalytic environments such as vigorously stirred liquid phase reactions. On more conventional supports, high levels of friction may lead to attrition, effectively altering the surface area of the exposed metal catalyst (47). Moreover, the relatively lower mechanical stability of common commercial carbon-based supports initiates the formation of fine particulates during operation. The existence of a large amount of micropores can reduce the full accessibility of the reactant particles to the active site.

The high strength of CNTs results from the covalent sp² bonds, which form a honeycomb lattice between the individual carbon atoms. In 2000, a MWCNT was tested and found to have a tensile strength of 63 GPa (51). A SWCNT has been shown to be the strongest material synthesised to date with a Young’s modulus of ca. 1 TPa (52).

Reactivity and Stability
Carbon supports are often unreactive and stable in many acidic and basic media, and consequently find use in a wide range of industrial applications (3, 53) while many other supports are rendered useless after reaction. However, traditional carbon-based supports have limitations not only when it comes to mechanical stability but also in terms of resistance to oxidising atmospheres at high temperatures (47). Oxidation and hydrogenation processes can result in gasification when the temperature is above 500ºC and approximately 700ºC, respectively (5). The order of ease of oxidation is: amorphous carbon > MWCNTs > SWCNTs. SWCNTs are generally more structured and have fewer surface defects than MWCNTs, and hence are more stable under most conditions (4).

AC is more easily oxidised than CNTs (4), and CNTs are more easily oxidised than graphite. Chiang et al. showed by thermogravimetric analysis (TGA) that acid oxidised MWCNTs were more thermally stable than AC fibres or C₆₀ fullerene (54). However, impurities in carbonaceous supports, such as metal residues from CVD processes, as well as defects in the structure, may not only limit the temperature at which hydrogenation takes place, but may also poison the active metal catalyst, such as Pd, and lower the temperature at which carbon oxidises (4). CNTs have good thermal conductivity and therefore reactions catalysed by metal/carbon systems need to be carefully controlled, especially if they are exothermic. Temperature can affect the performance of the catalyst on the carbon support and more research is needed to explore this aspect.
The effect of microwave irradiation on MWCNTs has been studied by Olivier et al. (55). The authors prepared 10 wt% Pd on MWCNTs with metal particles found only on the outer walls. Microwave irradiation was used to drive the hydrogenation of cinnamate esters with ammonium formate as a reductant. Chemoselective C=C bond hydrogenation occurred for all substrates and the catalyst could be recycled more than five times without loss of activity. The same reaction carried out under the same conditions with Pd/AC generated a variety of other products due to microwave degradation of chemical species, demonstrating that Pd/AC is less regio- and stereoselective than 10 wt% Pd on MWCNTs.

Liang et al. investigated the hydrogenation of carbon dioxide catalysed by supported palladium/zinc oxide catalysts (56). Pd/ZnO on MWCNTs proved more favourable than Pd/ZnO on either alumina or AC, with the MWCNTs providing a promoting effect. Also, herringbone-type MWCNTs had a greater promoting activity than parallel-type MWCNTs in these studies. The high conversion and selective formation of methanol from CO₂ by the MWCNT-supported catalysts was due to their favourable ability to reversibly adsorb a greater amount of hydrogen, thus increasing the rate of surface hydrogenation reactions.

**Surface Area and Selectivity**

SWCNTs, which are inherently microporous, are considered by some to be very suitable supports for metal catalysts. One reason for this is the high surface-to-volume ratio of SWCNTs compared to other supports. They also have high surface areas, 1587 m² g⁻¹ (57) (see Table I) after purification and tube end opening. The SWCNT structure is such that every atom is exposed to not one but two surfaces – both the inner and outer surfaces of the nanotube. Table I shows the approximate surface areas of various carbon supports. In the case of AC, the micropores are large in quantity and their size may actually slow the progress of substrate molecules into the pores (47). The ACs can have macro-, meso- and micropores, which can decrease the reproducibility of metal loading. Surface areas can range from 800–1200 m² g⁻¹ (3). However, the loading of Pd on the SWCNTs has been found to be lower than that obtained on MAXSORB® AC for hydrogen sorption studies (58). The authors of that study suggest that this is due to the larger pore volumes and surface area of the AC, and thus the correspondingly larger number of sites on which nucleation can occur. However, smaller Pd crystallites were formed on SWCNTs than on AC.

It has been shown that Pd’s activity for the hydrogenation of α,β-unsaturated aldehydes is high, but its selectivity remains challenging and many times it has been boosted by the addition of promoters (59). A much researched model compound of this class of aldehydes is cinnamaldehyde. Pd’s selectivity for cinnamyl alcohol is low when compared to Pt or ruthenium, however, using CNTs as supports seems to

### Table I

**Comparison of the Surface Areas of Carbon-Based Supports**

<table>
<thead>
<tr>
<th>Support</th>
<th>Typical surface area, m² g⁻¹</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated carbon</td>
<td>800–1200</td>
<td>(3)</td>
</tr>
<tr>
<td>Carbon black</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Conventional</td>
<td>100–1500</td>
<td>(3)</td>
</tr>
<tr>
<td>Graphitised</td>
<td>60–300</td>
<td>(3)</td>
</tr>
<tr>
<td>Graphite</td>
<td>10–50</td>
<td>(3)</td>
</tr>
<tr>
<td>Shaped carbon nanomaterials</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SWCNTs</td>
<td>1587ᵃ</td>
<td>(57)</td>
</tr>
<tr>
<td>MWCNTs</td>
<td>400ᵇ</td>
<td>(62)</td>
</tr>
<tr>
<td>Other</td>
<td>Timers 1587ᵃ</td>
<td>(117)</td>
</tr>
</tbody>
</table>

ᵃ After (i) debundling with DMF/EDA; (ii) acid treatment; (iii) wet oxidation
ᵇ After basic treatment

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provide advances in overcoming this challenge. Corma et al. compared Pd/SWCNTs with Pd/AC prepared by the same method (60). They showed that Pd/AC had higher activity for the hydrogenation of cinnamaldehyde to 3-phenylpropanaldehyde than Pd/SWCNTs. However, there was a wider range of particle sizes for Pd/AC than for Pd/SWCNTs. This was thought to be due to the larger variety of functional groups on AC. This may cause Pd ions not to be uniformly deposited in the beginning stages of deposition, resulting in bigger agglomerates over time, and hence a larger range of sizes.

MWCNTs are inherently mesoporous structures. The pore sizes of MWCNTs allow for diffusion, reaction and desorption of chemical species and thus are good supports for catalysts (61). They also possess high surface areas, reaching up to approximately 400 m² g⁻¹ after basic treatments (62). These supports sometimes give better activity than microporous supports such as AC. Janowska et al. showed that selectivity for the C=O bond hydrogenation product of cinnamaldehyde can exceed 80% when performed over Pd/CNTs (63). The explanation given was the lack of micropores as well as the high surface area of the CNTs. Lack of micropores affects the time spent by reactants and products on the support surface as well as affecting the manner in which desorption occurs. Also, Pd crystallites and CNTs may interact to alter the adsorption and selectivity properties.

In other research, Pd NPs inside MWCNTs and on AC both achieved complete conversion of cinnamaldehyde, although the completion times for the former were slightly faster (64). In this work it was shown that at a higher hydrogen flow rate, the rate of hydrogenation increased, but more so for the AC support than for the MWCNTs. The MWCNT-supported catalyst hydrogenated predominantly the C=C bond, rather than the C≡O bond, with only about 10% of the totally hydrogenated product forming. The AC-supported catalyst showed an equal selectivity for both products. Neither catalyst showed any selectivity for cinnamyl alcohol. It was concluded that the MWCNT-supported catalyst was superior in terms of selectivity for hydrocinnamaldehyde and that the MWCNTs had a higher surface area (some micropores on the traditional support being inaccessible to some substrates), resulting in a higher catalytic activity.

Zhang et al. used MWCNTs with different Pd loadings for benzene hydrogenation (43). They then compared the results with those from Pd/zeolite (SiO₂: Al₂O₃ = 5.1) and Pd/AC prepared under the same conditions. They showed that benzene conversion to cyclohexane approximates 100% at the highest loading (12.0 wt%) Pd/MWCNT. An intermediate loading (8.0 wt%) yielded nearly double the conversion of benzene compared to that achieved using the AC- or zeolite-supported catalysts. This was despite the fact that the specific surface area of the MWCNTs was lower than those of the zeolite and AC as determined after acid treatment. It was also shown that diluted Pd salt solutions yielded smaller Pd particles inside tubes and more concentrated solutions yielded larger particles, which would influence catalytic rates.

In a study on the partial hydrogenation of phenylacetylene, CNT, AC and carbon black were used as supports for Pd (65). Although all active phases achieved over 95% conversion to styrene, the selectivity was highest for the Pd/CNT catalyst, with five runs maintaining the activity and selectivity. The AC support showed agglomeration of the Pd NPs.

Pd/CNFs (5 wt% Pd) and Pd/AC were used in the liquid phase hydrogenation of the C=C bond in cinnamaldehyde by Pham-Huu et al. (6). Both the surface area:volume ratio and thus catalytic activity were higher for the CNF-supported catalyst. This was assumed to be due to the larger number of micropores on AC leading to diffusion problems which affect the catalytic rate. This cannot occur in CNFs because they have no micropores. Pd/CNFs produced almost exclusively (98%) hydrocinnamaldehyde and negligible amounts of cinnamyl alcohol and 3-phenylpropanol, showing that the selectivity of the catalyst for C=C hydrogenation under these conditions was good. The AC catalyst produced a mixture of all products. However, the nature of the carbon support was shown to have negligible effect on the hydrogenation of a variety of polar aromatic compounds in a recent article by Anderson et al. (66). They showed that the nature of the solvent is a bigger factor in selectivity.

Graphite has a comparatively low surface area (10 to 50 m² g⁻¹), although grinding processes can increase it up to approximately 300 m² g⁻¹ (3). The capacity for adsorption of volatile organic compounds onto MWCNTs and CNFs is lower than for high surface area graphite (67).

**Recovery and Recycling of Precious Metals**

The high price of precious metals makes the recovery and reuse of such catalysts economically important. Carbon supports make recovery more economical compared to metal oxide supports as they can be burnt off the metal catalyst and the catalyst recovered.
from a small volume of ash. The solid waste is minimal. The metal can then be dissolved and recovered from acidic solutions.

Oxidation of AC over long periods of time can decrease its usefulness as a support (3). The inertness of CNTs, on the other hand, enables them to resist oxidation over long periods of time and allows them to be recycled many times. CNT-metal hybrids can be dispersed to a fairly uniform degree by stirring in organic solvents. After use, the hybrid CNT-NPs can be recovered by gravitational sedimentation. Hence, as a support, CNTs are economical and stable when it comes to the processes of recovery and reuse of catalysts.

**Loading Techniques and Considerations**

A fair amount of research has gone into mechanisms suitable for attaching Pd NPs to the walls of SWCNTs and MWCNTs (68). Common loading techniques for Pd include impregnation (42, 43, 64), deposition precipitation (69), electroless deposition (70, 71) and electrochemical deposition (72, 73). Less commonly used methods include CVD (74) and microemulsion techniques (75). Supercritical CO₂ has been used instead of conventional solvents to effect a greener approach to Pd loading techniques (76). However, the Pd NP size, crystal structure and distribution cannot be accurately manipulated by many of these processes.

Considerations for choosing a loading technique include the desired level of Pd loading, required particle size and/or size distribution ranges, and the macroscopic distribution of particles on the support. The higher the Pd loading, in general, the greater the rate of product formation, since more Pd catalyst particles are exposed to substrate molecules. Most methods yield heterogeneously dispersed particle sizes, although controlling the size of metal particles is still being investigated. Typically, the smaller the particle size, the larger the surface area of Pd metal and the higher the catalytic activity. Pore structure and accessibility of the substrate to the metal in the pores also influences the macroscopic distribution. The most common types of supported catalyst structure are eggshell, uniform distributions or intermediates of the two (3). Typically, uniform distribution of small metal NPs is ideal for hydrogenations. However, uniformly impregnated catalysts are more likely to lose part of the Pd metal loading through leaching (3). This can be minimised by improving the availability of hydrogen in the liquid reaction medium and by either using less catalyst for the reaction or decreasing the Pd metal loading.

Pristine CNTs are considered to be relatively inert, allowing for only low levels of Pd deposition (4) at defect sites such as Stone-Wales defects, dangling bonds at open tips and vacancies (77). The CNTs do not contain many functional groups on their surfaces and thus need to be activated to create anchoring sites for better Pd metal deposition. Many of these techniques are similar to the pretreatment of other carbon supports and are primarily used to remove metallic impurities, such as iron derived from the CNT synthesis, and generate surface groups in the process. Functionalisation can be done through ball milling (78) or by chemical or electrochemical means. Chemical means often incorporate the use of highly oxidising conditions such as sulfurous or nitric acid (79–81) or molecular oxygen (79). Sometimes sonication is used in conjunction with a chemical means (82). Plasmas can also be employed (79, 83, 84). Covalent functional groups such as alcohols (–OH), carbonyl groups (–C=O) and carboxylic acids (–COOH) form.

In general, more oxygen groups aid higher dispersion of Pd, although some authors maintain that oxygen-containing groups are not sites onto which the metals anchor, but rather that they merely increase wetting. Enhanced wetting allows for better dispersion in aqueous deposition solutions. Unger et al. achieved very low loadings of Pd (1 wt%) on pre-oxidised CNTs (85). They suggest that covalent bonding does not occur between the oxide groups and the metal, and that Pd therefore cannot attach in large quantities. However, Guo et al. suggested that more Pd particles form at positions where –COOH groups would preferably form, for example at the end of SWCNTs (86).

Most reports discuss Pd NPs decorated on the exterior of CNT surfaces. However, some state that certain Pd metal catalysts loaded on the inside of nanotubes exhibit a higher catalytic activity than the same amount on more conventional supports (43, 87). Figure 4 shows a transmission electron microscopy (TEM) image of such a system. The supposition is that the partial pressure of the substrates inside the tubes is increased, altering the rate of catalysis. Factors affecting the placing of Pd particles inside tubes include the hydrophobicity of tubes, the inner diameter, the concentration of the Pd in the precursor solution and the surface tension of the Pd deposition solution. Pd particles found near the tips of tubes were probably deposited there due to the fast rate of evaporation of water out of the tubes. The strong interaction
between Pd particles and the tube could give rise to the faceted nature of the catalyst particles (87). It has been suggested that this interaction may affect dispersion (43). Tessonnier et al. suggest that the morphology of the inner wall may alter the electronic nature of the adsorbed metal and thus modify the adsorption of the substrate and selectivity for the product (64). They stated that the nature of the precursor solution seemed to have a negligible effect on dispersion.

Factors influencing the properties of the nanometallic particles include size, shape and crystalline geometry (88). Computational calculations indicated that CNT-supported Pd clusters would have a higher activity than the unsupported cluster for H2 bond breaking in hydrogenation reactions, (89). Franklin et al. reported the first controlled decoration of SWCNTs with Pd particles of a consistent morphology (90), and Ansón et al. found that the mass ratios of the Pd: support (SWCNTs or MAXSORB® AC) directly determined the percentage of Pd loaded (58). These latter authors suggested, from their results, that a threshold for Pd saturation is reached when the mass ratio of support:Pd is 1:4. Also, the crystallite size was larger at higher Pd loadings. These authors demonstrated that the quantity of Pd loaded onto the SWCNTs was not altered in runs that used oxidative pretreatments, although their Pd wt% loading values decreased slightly after a nitric acid treatment in the case of Pd[PPh3]4 as the Pd source. Different precursor Pd compounds were also found to influence the loading on CNTs and AC in the same studies.

**Modified CNTs as Supports**

Besides modification with oxide groups, other means of functionalisation can produce further benefits. Functionalisation can be covalent (91) or non-covalent (92). CNTs have the ability to attach a wide range of chemical species at active sites, such as their sidewalls, tubular tips or defect areas. Exohedral and endohedral functionalisation can also provide an opportunity to create unique catalyst supports for Pd.

Agglomeration of NPs reduces the surface area of catalytically active metal particles. Some loading techniques, such as modification of the support with a surfactant or an an ionic liquid (IL) before metal deposition, can be employed to control the formation of larger nanoclusters on the surface of CNTs. Surface moieties are thought to aid stabilisation of the crystallites during sintering (3). Chun et al. functionalised MWCNTs with an imidazolium bromide followed by Pd (93). They effectively formed an IL catalytic system rendering the functionalised MWCNTs soluble in water, and thereby successfully prevented CNT agglomeration and aided dispersion in the aqueous phase ready for Pd deposition. Following this, hydrogenation of trans-stilbene was performed with turnover frequency (TOF) values up to 2820 mol h⁻¹, which is considered to be high. Varying the anion was shown to influence the catalytic activity in this hydrogenation reaction. Pd/IL-MWCNTs (where f indicates functionalised; IL is [1-butyl-3-methylimidazolium][hexafluoroantimonate]) remained active after 10 cycles and were then used in olefin hydrogenations. Only after 50 runs did the activity significantly decrease.

Sodium dodecyl sulfate (SDS) (94) and sodium bis(2-hexylethyl)sulfosuccinate (AOT) (75) also aid in the homogenous distribution of Pd particles on the support by acting as surfactants. Agglomeration of Pd particles is prevented. Figures 5(a) and 5(b) show Pd/CNTs prepared with and without AOT, respectively (75). The fairly even distribution of NPs in Figure 5(a) is apparent, whereas Figure 5(b) shows significant agglomeration. SDS (95) and sodium n-tetradecyl sulfate (SC₄S) (96) also induce reduction of the Pd precursor. Karousis et al. used Pd/MWCNTs with SDS to hydrogenate a variety of olefins (97). Four olefins were successfully hydrogenated. The Pd/MWCNTs were then compared to Pd/AC for the hydrogenation of methyl1-octadecenoate and 2-methyl-2-pentenal.

**Fig. 4. TEM image of Pd NPs located primarily on the inside of MWCNTs with the arrowheads indicating the presence of some highly faceted Pd particles (87) (Reproduced by permission of Elsevier)**

**Figures 5(a) and 5(b) show Pd/CNTs prepared with and without AOT, respectively (75). The fairly even distribution of NPs in Figure 5(a) is apparent, whereas Figure 5(b) shows significant agglomeration. SDS (95) and sodium n-tetradecyl sulfate (SC₄S) (96) also induce reduction of the Pd precursor. Karousis et al. used Pd/MWCNTs with SDS to hydrogenate a variety of olefins (97). Four olefins were successfully hydrogenated. The Pd/MWCNTs were then compared to Pd/AC for the hydrogenation of methyl1-octadecenoate and 2-methyl-2-pentenal.**
The molar ratio of Pd:substrate was kept constant. TOF values for Pd/MWCNTs for both compounds were 3 to 5 times higher than for Pd/AC. Large amounts of the Pd precursor also cause agglomeration. Thus it is important to control the amounts of both the precursor and the SDS added to the reaction mixture for optimal dispersion (94).

In another paper, Pd was loaded onto SDS-stabilised MWCNTs and SWCNTs and then used in successful hydrogenations of the same four olefins as well as 3-phenyl-2-propenal (98), although a detailed comparison of the two supports was not given. The Pd/MWCNTs were then compared with Pd/AC for the hydrogenation of methyl-9-octadecanoate and 2-methyl-2-pentenal. TOF values for Pd/MWCNTs approximated 3 to 5 times higher than for the conventional catalyst. Even after 7 cycles of the Pd/MWCNTs there was little to no leaching of Pd off the support.

Doping of CNTs has been fairly extensively researched for N- and B-dopants (99–101) resulting in modified properties. Many properties such as electronic properties (102) and even the strength with which other species adsorb (103) are affected by doping. Most CNT doping studies have been carried out for MWCNTs, with a few on SWCNTs for applications such as field emission devices. Generally, CNTs are inert, but the incorporation of heteroatoms into their structure can give rise to a more chemically active material. Disadvantages include the fact that often N-doped counterparts are less thermally stable and more prone to oxidation (104). The nitrogen incorporation can greatly alter the morphology of the CNTs (104, 105), although in some cases no morphology change was observed (101).

Graphitisation was found to be enhanced in B-doped MWCNTs (106). An and Turner studied the binding between transition metals and CNTs by making use of density functional theory (DFT) calculations for individual metal atoms on N- or B-doped SWCNTs at chosen sites (103). These initial studies showed, among other things, that a range of commercially important transition metals, including Pd, undergo higher chemisorption with doped SWCNTs as opposed to pristine SWCNTs. B-doped CNTs gave the most enhanced binding. Amadou et al. carried out experiments in which the dispersion of Pd was found not to be significantly different on doped or undoped tubes (42). However, it was interesting to note that no Pd NPs were found inside the N-doped tubes. This was thought to be due to compartmentalisation as shown in Figure 6. The Pd/N-doped CNTs were compared with Pd/CNTs and Pd/AC for the liquid phase hydrogenation of cinnamaldehyde. Pd/AC, with the highest specific surface area, displayed the highest activity. Pd/N-doped CNTs had an activity nearly equal to that of Pd/AC, but almost double that of the undoped Pd/CNTs. This indicated a significant influence of the N incorporation on the activity of the catalyst for C=C bond hydrogenation. In terms of selectivity, the doped support was best for hydrocinnamaldehyde production while the Pd/AC catalyst was the least selective.

**Bimetallic Catalysts – Effect of Secondary Metal**

Research has shown that bimetallic catalysts can influence the catalytic activity of a system (107) and sometimes have higher catalytic performance in certain reactions than a single metal catalyst (108). The additional metal(s) can improve the size and

**Fig. 6. TEM showing the ‘bamboo’ cross-structures in a Pd loaded N-doped MWNT without Pd NPs incorporated inside the cavities (42)** (Reproduced by permission of Elsevier)
morphism of active particles as well as the catalyst selectivity (108).

The activity of palladium-platinum is superior to that of other commercial bimetallic catalysts in the hydrogenation of aromatic compounds, a pre-step in the desulphurisation of fuels. Noble metals are susceptible to poisoning by sulfur. Use of acidic supports or bimetallic Pd-Pt catalysts has proven to enhance the resistance to poisoning by sulfur (109). Pawelec et al. studied Pd-Pt/MWCNTs in the hydrogenation of toluene and naphthalene in the presence of dibenzothiophene in the gas phase to monitor, simultaneously, the hydodesulphurisation of the sulfur-containing compound (110). A Pd-Pt/zirconium phosphate–silica zeolite and a Pd-Pt/amorphous SiO₂–Al₂O₃ (ASA) catalyst were also prepared for comparison although different loading techniques were used. The results suggested that all catalysts were more active for toluene hydrogenation than for the polyaromatic compound. Pd-Pt/MWCNTs had the lowest loading and BET specific areas but the highest activity for toluene hydrogenation. However, Pd-Pt/ASA was the best catalyst for naphthalene hydrogenation and the hydodesulphurisation of dibenzothiophene. The combined effect of the Pd-Pt alloy may be a factor, coupled with the location of these NPs on the MWCNTs, since a marked lack of steric hindrance for the substrate would be found on the outer surfaces of MWCNTs as compared to the other catalysts. However, the bimetallic effect is still not yet well understood.

Qiu et al. observed that the conversion and selectivity towards cinnamyl alcohol was highest for a Pd-Ru bimetallic catalyst on CNTs than for either of the two monometallic catalysts under identical conditions (111). This finding was attributed either to Ru's promoting effect on Pd or to a combined enhanced effect from Pd and Ru together.

Arene hydrogenation is important in industry, for example, for diesel fuels with low aromatic contents. Heterogeneous catalysis with metals at high temperatures is the traditional method for arene hydrogenation. Yoon et al. hydrogenated benzene at room temperature under 1–20 atm over palladium-rhodium/ CNTs (112). A high activity for benzene reduction, with no solvent, was found. Commercially available Pd/C and Rh/C cannot do this under these conditions yet. Pd/CNT had very low or no activity at room temperature, whereas the Pd-Rh/CNT had a catalytic activity much higher than either of the monometallic systems. A conversion of 98% of benzene to cyclohexane occurred after 24 h at room temperature and 10 atm. Pd/CNT needed 24 h at 50°C and 10 atm to achieve a near 50% conversion of benzene to the saturated product. Pd-Rh/CNT was shown to be recyclable multiple times.

Functionalised MWCNTs in a water-in-hexane microemulsion with a surfactant were loaded with Pd, Rh or Pd-Rh (75). Arene hydrogenation tests revealed that Pd-Rh/CNTs (see Figure 7) were more active than the monometallic systems for anthracene hydrogenation. However, the detailed morphology of this bimetallic catalyst system was not studied or confirmed.

It has also been shown that the molar ratio of the two metals in a bimetallic oxide catalyst, such as Pd/ZnO, has influence on the catalytic activity of CO₂ hydrogenation (56).

**Hydrogenation on Palladium/CNT Catalysts**

Palladium on CNT supports is effective as a catalyst for the reduction of a variety of functional groups. Below are specific examples for carbon–carbon multi-bond and nitrogen-containing group hydrogenations.

**Alkene and Alkyne Hydrogenation**
Pd/CNTs grown and supported on carbon microfibres were used as catalysts in the gas phase hydrogenation of cyclooctene (74). Initial studies showed the system to be active for the reduction of this alkene.

The first report of the use of Pd/CNT to hydrogenate C=C discussed the successful hydrogenation of tolane, phenylacetylene and 1-heptyne with 5% Pd on CNTs (113). The results showed that only 0.02 mol% Pd/CNT was needed to convert all the starting materials to products, indicating that this catalytic system had a high activity towards C=C hydrogenation. This catalytic activity was higher than that found in earlier work by the same authors for the hydrogenation of toluene over Pd complexes supported on fullerenes (114). The ratio of the two reaction products was found to be determined largely by the temperature and length of time of hydrogenation. The lower the hydrogenation time, or the higher the temperature (within the range 22–60°C), the greater the conversion to a...
saturated product. Further reactions with the Pd/CNT catalyst showed the same catalytic performance. All three acetylenic hydrocarbons underwent complete conversion to a mixture of ethylenic and saturated compounds. Replication of the catalyst at 60°C for 7 h yielded 100% selectivity for the saturated product.

Jung et al. studied Pt on CNFs and CNTs for cinnamaldehyde hydrogenation and Pd on CNFs for 1-octyne hydrogenation (115), amongst other supports. They used a colloidal microwave process to load metals onto supports. This method makes pretreatment unnecessary and yields a high dispersion of the catalyst. Unloaded supports (CNFs, CNTs, AC and Al2O3) were tested for cinnamaldehyde catalysis but no activity was found. Pd is possibly the most selective catalyst for the semi-hydrogenation of alkynes. Previous studies had shown the hydrogenation of cinnamaldehyde over Pt/CNTs to be poorer than over Pt/CNFs, thus only CNFs were used in the 1-octyne studies. Conversion of 1-octyne by Pd on two types of CNFs yielded the semi-hydrogenated product 1-ocene, which had a slow conversion to the saturated product.

Conversion of Nitro to Amino Group via Hydrogenation

Pd/AC is a common catalyst for the selective hydrogenation of nitrobenzene and derivatives thereof. In one study, nitrobenzene was hydrogenated in the liquid phase by using Pd deposited on the inside of MWCNTs (87). This reaction was compared with a Pd/AC system. The activity of the Pd/MWCNT catalyst hybrid was superior to that of the Pd/AC catalyst system, even though the surface area of the AC was higher than that of the MWCNTs. The observed results were explained in terms of the lack of micropores in the MWCNTs. It was also suggested that convection in the liquid phase in the MWCNTs increased the rate of substrate collision with H2 molecules and thereby increased the activity.

Jiang et al. hydrogenated the nitro group of o-chloronitrobenzene to provide an amine derivative using Pd supported on three different supports: CNFs, γ-Al2O3 and SiO2. (116). Both the activity and selectivity for the formation of the amine product were favoured by the CNT-based catalyst. These results may be influenced by the geometric and electronic effects of CNTs on the catalytic process as well as the textures and properties of the CNTs.

Hydrogenation of Nitric Oxide

Wang et al. used pre-hydrogenated Pd/CNTs to reduce NO (44). The reducing action of the hydrogenated Pd/CNT showed that such systems can take up hydrogen effectively in significant amounts. This may also be of interest to the hydrogen storage industry. CNTs without a metal additive were hydrogenated to a far lesser extent. Subsequent addition of NO caused reduction of this gas in only the Pd/hydrogenated CNTs.

Many examples of Pd/CNTs and bimetallic pgm/CNTs as hydrogenation catalysts are found in the literature. Table II summarises some of this research.

Conclusions

This survey of the literature has shown that the catalytic activity of nanosized Pd metal particles in hydrogenation reactions is greatly influenced by the support on which this metal is loaded. CNTs may be highly advantageous as supports compared with the more traditional carbonaceous supports. CNTs do not display many of the disadvantages that the more common commercial supports possess. In particular, CNTs have very high mechanical strength and thus are preferable over other supports in mechanically taxing stirred batch reactions. In terms of surface area, SWCNTs, in particular, have very high surface areas and are inherently microporous. Their high surface areas also allow for more reproducible loading compared to some of the currently used ACs. CNTs lower the rate of metal NP agglomeration, due to the strong metal–support interaction arising from the unique curvature of the CNTs, thereby enhancing the lifespan of the catalyst and ensuring its high level of activity. The chemical stability of CNTs makes them less easily oxidised than ACs, and they are economical and stable when it comes to the recovery and reuse of catalysts.

In many cases the chemoselectivity of Pd/CNTs in hydrogenation reactions has been shown to be superior to Pd/AC systems. One study showed that surfactant-modified Pd/MWCNTs gave higher TOF values for hydrogenation than the equivalent Pd/AC hybrids. Almost double the activity and a superior selectivity for a specific product was found for Pd/N-CNTs compared to undoped Pd/CNTs and a Pd/AC catalyst, respectively, in a study on hydrogenation reactions.

Studies of bimetallic Pd systems on CNTs revealed that selectivity and conversion for the hydrogenation of selected bonds, as well as activity towards hydrogenation of certain substrates, is enhanced by the presence of a secondary metal.

In summary, evidence exists for the superior activity and selectivity of Pd/CNTs in a range of hydrogenation reactions. There is also evidence for improved catalytic performance in certain cases by the use of...
## Table II

Examples of Palladium and Platinum Group Metal Bimetallic Catalysts Supported on Carbon Nanotubes Used in Hydrogenation Reactions

<table>
<thead>
<tr>
<th>Metal-catalyst system</th>
<th>Substrate for hydrogenation</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monometallic catalyst</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pd/CNTs</td>
<td>Cinnamaldehyde</td>
<td>(60)</td>
</tr>
<tr>
<td>Pd/SWCNTs</td>
<td>NO</td>
<td>(44)</td>
</tr>
<tr>
<td>Pd/MWCNTs</td>
<td>NO</td>
<td>(44)</td>
</tr>
<tr>
<td>Pd/MWCNTs</td>
<td>Benzene</td>
<td>(43)</td>
</tr>
<tr>
<td></td>
<td>Cinnamaldehyde</td>
<td>(47, 63, 64)</td>
</tr>
<tr>
<td></td>
<td>trans-Stilbene</td>
<td>(76)</td>
</tr>
<tr>
<td></td>
<td>Cyclooctene</td>
<td>(74)</td>
</tr>
<tr>
<td></td>
<td>Nitrobenzene</td>
<td>(87)</td>
</tr>
<tr>
<td></td>
<td>Phenylacetylene</td>
<td>(65)</td>
</tr>
<tr>
<td></td>
<td>Cinnamate esters</td>
<td>(55)</td>
</tr>
<tr>
<td></td>
<td>Tolane, phenylacetylene, 1-heptyne</td>
<td>(113)</td>
</tr>
<tr>
<td></td>
<td>o-Chloronitrobenzene</td>
<td>(116)</td>
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<tr>
<th>Metal-catalyst system</th>
<th>Substrate for hydrogenation</th>
<th>References</th>
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<tbody>
<tr>
<td>Pd/CNFs</td>
<td>Cinnamaldehyde</td>
<td>(6)</td>
</tr>
<tr>
<td></td>
<td>1-Octyne</td>
<td>(115)</td>
</tr>
<tr>
<td></td>
<td>Benzoic acid, benzaldehyde, acetophenone, benzamide, phenylacetic acid, cinnamic acid, 4-hydroxybenzoic acid</td>
<td>(66)</td>
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<table>
<thead>
<tr>
<th>Bimetallic catalyst</th>
<th>Substrate for hydrogenation</th>
<th>References</th>
</tr>
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<tbody>
<tr>
<td>Pd/ZnO-(h)-MWCNTs</td>
<td>CO(_2)</td>
<td>(56)</td>
</tr>
<tr>
<td>Pd/ZnO-p-MWCNTs</td>
<td>CO(_2)</td>
<td>(56)</td>
</tr>
<tr>
<td>Pd-Ru/CNTs</td>
<td>Cinnamaldehyde</td>
<td>(111)</td>
</tr>
<tr>
<td>Pd-Pt/MWCNTs</td>
<td>Toluene/naphthalene/dibenzothiophene</td>
<td>(110)</td>
</tr>
<tr>
<td>Pd-Rh/MWCNTs</td>
<td>Benzene</td>
<td>(112)</td>
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(Continued)
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<tr>
<th>Metal-catalyst system</th>
<th>Substrate for hydrogenation</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modified CNTs with monometallic catalyst</td>
<td>Pd/SDS-MWCNTs</td>
<td>Methyl-9-octadecanoate, 2-methyl-3-butene-2-ol, 3,7-dimethyl-2,6-octadien-1-ol, 2-methyl-2-pentenal</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Methyl-9-octadecanoate, 2-methyl-3-butene-2-ol, 3,7-dimethyl-2,6-octadien-1-ol, 2-methyl-2-pentenal, 3-phenyl-2-propenal</td>
</tr>
<tr>
<td>Modified CNTs</td>
<td>Pd/SDS-SWCNTs</td>
<td>Methyl-9-octadecanoate, 2-methyl-3-butene-2-ol, 3,7-dimethyl-2,6-octadien-1-ol, 2-methyl-2-pentenal, 3-phenyl-2-propenal</td>
</tr>
<tr>
<td></td>
<td>Pd/imidazolium salt-MWCNTs</td>
<td>trans-Stilbene</td>
</tr>
<tr>
<td></td>
<td>Pd/sodium bis(2-hexylethyl)-sulfosuccinate-MWCNTs</td>
<td>Anthracene</td>
</tr>
<tr>
<td>Bimetallic-surfactant composite</td>
<td>Pd-Rh/sodium bis(2-hexylethyl)-sulfosuccinate-MWCNTs</td>
<td>Anthracene</td>
</tr>
<tr>
<td>Doped</td>
<td>Pd/N-MWCNTs</td>
<td>Cinnamaldehyde</td>
</tr>
</tbody>
</table>

*a SWCNTs = single-walled carbon nanotubes
*b MWCNTs = multi-walled carbon nanotubes
*c CNFs = carbon nanofibres
*d h = herringbone-type
*e p = parallel-type
*f SDS = sodium dodecyl sulfate
modified or bimetallic Pd/CNT systems. Such findings will, hopefully, spur on research in this field. However, ACs are still widely chosen as hydrogenation supports due to their ease of preparation and low cost. The challenge remains of improving the cost-effectiveness of CNT synthesis to make them an economically viable alternative to ACs as Pd supports for hydrogenation reactions.

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Palladium-Polyaniline and Palladium-Polyaniline Derivative Composite Materials

A BRIEF OVERVIEW OF THEIR PREPARATION AND POTENTIAL APPLICATIONS

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Palladium nanoparticles of different sizes and shapes combined with polyaniline and derivatives of polyaniline can give rise to a host polymer with interesting physical properties and important potential applications. The resulting composite can be produced in the form of nanofibres, nanorods, thin films, etc. Potential applications of this composite material for catalysis and sensor systems are discussed.

One key property distinguishing classical polymers from metals is their low electrical conductivity. A new class of organic polymers capable of conducting electricity has recently been developed (1, 2). These polymers become conductive upon partial oxidation or reduction, a process commonly referred to as ‘doping’. The electrical properties of conductive polymers can be changed reversibly over the full range of conductivity from insulators to metallic conductors. Their potential as novel materials in value-added industrial and consumer products is opening up wholly new avenues of application for polymer materials.

Among conducting plastics, polyaniline has become a particular focus of interest because of its environmental stability (3), controllable electrical conductivity (4), and interesting redox properties associated with the chain nitrogen (5). The electrical properties of the aniline polymers can be improved substantially by secondary doping (6). Polyaniline compounds can be designed to achieve the particular conductivity required for a given application. The resulting blends can be as conductive as silicon and germanium or as insulating as glass. Additional advantages are that the compound can be mixed simply with conventional polymers, and it is easy to fabricate polyaniline products into specific shapes. The conductivity of polyaniline makes it an ideal shield against static electric discharges, and as a consequence polyaniline compounds have been used in the packaging of electronics products. Polyaniline compounds are being tested for use as protective materials against electromagnetic radiation. Further, scientists hope that one day printed circuit boards, electrochromic windows in houses and cars, and conductive fabrics will contain polyaniline compounds.

The presence of a number of intrinsic redox states (Figure 1) has substantially increased the number of potential applications of aniline polymers for use in practical devices. The aniline polymers have a general formula of the type \([(-B\text{--NH--B--NH--})_y \text{--}(\text{B--N=Q=N--})_y]_x\), in which B and Q denote respectively the benzene and the quinoid forms. In polyaniline, the neutral intrinsic redox states (Figure 1) can vary from that of the fully oxidised pernigraniline (PNA; \(y = 0\)), to that of the...
fully reduced leucoemeraldine (LM; \( y = 1 \)). The 50% intrinsically oxidised polymer has been named emeraldine (EM; \( y = 0.5 \)), and the 75% intrinsically oxidised polymer is named nigraniline (NA; \( y = 0.75 \)) (2). The synthesis and characterisation of polyaniline have been reviewed previously by Geniès et al. (7), Lux (8) and Gospodinova et al. (9). Polyaniline is a member of the semi-flexible rod polymer family. The synthesis and characterisation of electroactive polymers have become two of the most important areas of research into polymers, as well as in materials science over the past two decades.

Metal nanoparticles with different sizes and shapes can be combined with polyaniline to form hybrid materials. Hybrids represent a new class of materials that may combine desirable physical properties characteristic of both their organic and metallic components within a single composite. The metallic portion offers the potential for a wide range of electrical properties, substantial mechanical hardness and thermal stability, whereas the polymer part can provide high fluorescence efficiency, large polarisability, plastic mechanical properties, ease of processing and structural diversity.

The present article reviews both advances in methods of synthesis and application-related performance for various palladium-polyaniline and palladium-polyaniline derivative composite materials systems.

**Palladium-Polyaniline Composite Coating for LD Polyethylene**

Low-density polyethylene (LDPE) is a useful substrate for a wide range of laboratory experiments as well as many industrial applications (10–13). Although LDPE is a relatively inert substrate, it can be graft-copolymerised with acrylic acid to enhance the growth and adhesion of polyaniline coatings so as to achieve a thin conductive surface layer. In an earlier work, Neoh and coworkers (14) reported the formation of gold particles on the surface of a polyaniline film coated onto acrylic acid graft-copolymerised LDPE.

The thrust of this work was investigating how the electroactive polymer substrate was affected by the metal reduction process. The coating of LDPE films with a polyaniline-palladium composite layer was studied by Wang et al. (15). They used two methods for the synthesis of the polyaniline-palladium layer on the LDPE. Common to both was the initial step: the LDPE surface was first graft-copolymerised with acrylic acid to enhance the adhesion of the polyaniline-palladium layer. Subsequently, in the first method (Method 1 in Figures 2 and 3), polyaniline was deposited on the acrylic acid graft-copolymerised LDPE. This was followed by a reaction with palladium nitrate which resulted in a layer of palladium metal particles being deposited onto the polyaniline surface. In the
second method (Method 2 in Figures 2 and 3), polyaniline powder was first reacted with palladium nitrate. The powder was then treated with N-methylpyrrolidinone, after which it coated the acrylic acid graft-copolymerised LDPE. The latter method resulted in nanosized palladium metal particles being distributed in the polyaniline coating, rather than being confined to the surface of the polyaniline layer. In both methods, the palladium metal particles conferred surface conductivity on the LDPE substrate, even with the polyaniline in the undoped state. It was found that the polyaniline-palladium coating adhered excellently to the acrylic acid graft-copolymerised LDPE substrate at low palladium contents, but adhesion was weakened significantly at high palladium contents due to the palladium interfering with the interaction between the polyaniline and the acrylic acid graft-copolymerised chains. The polyaniline was synthesised in the reduced form, that is, leucoemeraldine (LM). The advantage of using LM is that it can very easily be oxidised, and palladium nitrate is reduced more rapidly.

X-ray photoelectron spectroscopy (XPS) analysis by Wang et al. (15) (Figure 2) of LM on acrylic acid graft-copolymerised LDPE after reaction with Pd(NO₃)₂ revealed two Pd 3d₅/₂ peaks at 335 and 338 eV, which are the characteristic peaks for the Pd(0) and Pd(II) species respectively. Initially, Pd(0) was the main oxidation state of palladium. For Method 1, the intensity of the Pd(II) peak increased with time, indicating that the Pd(II) species deposited on the surface of polyaniline without further reduction to Pd(0). By contrast, for the sample which was prepared using Method 2, XPS analyses confirmed that the Pd 3d₅/₂ peak at 335 eV was predominant throughout the reaction, while the peak at 338 eV did not show any significant incremental change as the reaction progressed. It was concluded that Pd(0) remained the predominant species on polyaniline for the sample which was prepared by Method 2. The disparity

\[ \text{Fig. 2 XPS Pd 3d spectra of LM on acrylic acid-graft copolymerised LDPE after reaction by Method 1 for: (a) 10 min; (b) 60 min; (c) 120 min; and (d) 180 min; and by Method 2 for: (e) 10 min; (f) 60 min; and (g) 180 min. Reproduced from (15) with permission from Elsevier} \]
between the amounts of deposition of palladium species for the two samples results from the difference in the surface area and the availability of the reaction sites.

Figure 3 shows the scanning electron microscopy (SEM) images for the two methods corresponding to the palladium(0)-polyaniline composite on the acrylic acid graft-copolymerised LDPE film after different reaction times. In Figure 3 for Method 1, the average particle size of 100 nm or less as estimated from these images does not increase substantially during the early stages, ~ 10 to 60 min (Figures 3(b) and 3(c)), of the reaction. After a reaction time of 180 min or more, the surface of the LM film was covered with palladium (Figure 3(d)). In contrast, for Method 2, during the initial stages of the reaction (~ 10 min, Figure 3(f)), at a Pd(II):N molar ratio of 1:5, the average particle size was about 70 nm. After 180 min (Figure 3(h)), the average particle size had increased by some 300%. This increase in size was a direct result of the increase in size of the palladium clusters accumulated on the surface of the polyaniline powder as the reaction progressed and the subsequent dispersion of the particles in the polyaniline-N-methylpyrrolidinone solution.

Chemical Deposition of Palladium on Polyaniline

The reaction of polyaniline in its lowest oxidation state, LM, with palladium chloride and palladium nitrate has been investigated by Wang et al. (16). Polyaniline was synthesised via the oxidative polymerisation of aniline by ammonium persulfate, and converted to emeraldine (EM) or 50% oxidised base by treatment with excess 0.5 M sodium hydroxide. The fully...
reduced form of the polyaniline, LM, was obtained by the reduction of the EM base with anhydrous 98% hydrazine for 3 h, followed by thorough washing with deionised water. The LM film obtained was then pumped dry under reduced pressure. Since the LM film is very easily oxidised, the palladium uptake experiments were conducted soon after the preparation of these films.

The LM film was used for the palladium uptake experiments using palladium chloride and palladium nitrate. The amounts of palladium deposited from the palladium precursors on the LM film are indicated in Figure 4. This figure shows that palladium nitrate reacts more effectively with LM than does palladium chloride, a finding that Wang et al. confirmed was reproducible. XPS measurements were performed to determine the state of the palladium deposited on the LM. Figure 5 shows the XPS Pd 3d spectra of the LM films after reaction in palladium chloride and palladium nitrate solutions for varying periods of time. For palladium nitrate, it is quite clear that Pd(0) is the principal state of the palladium deposited on the surface of the LM film. For palladium chloride, while Pd(II) was the predominant state on the LM surface at the beginning of the reaction, after 300 min, the Pd(0) state became the predominant species. Atomic force microscopy (AFM) images of the surface of the LM films after a 10 min immersion in palladium chloride and palladium nitrate solutions for varying periods of time.
Dium nitrate solutions are shown in Figures 6(a) and 6(b), respectively. A higher average roughness value, \( R_a \), was achieved for the film when it was treated in palladium nitrate, as a direct consequence of the larger amount of palladium deposited on this film.

**Electrochemical Behaviour of Polyaniline-Palladium Composite Films**

The electrochemical behaviour of polyaniline films containing palladium nanoparticles was investigated by Park et al. (17) when the films were immersed in a propylene carbonate solution. To prepare the polyaniline-palladium nanoparticle composite film, a preformed poly(N-vinyl-2-pyrrolidone) stabilised palladium nanoparticle colloid was dispersed in a N-methyl-2-pyrrolidone (NMP) solution. Then, polyaniline (36% oxidised state) was added slowly to the solution which was then stirred for 24 h. The resultant solution was cast on glassy carbon and dried under vacuum for 4 h at room temperature. This assembly was used as the working electrode. A platinum coil and Ag/Ag\(^{+}\) were used as the counter and reference electrodes, respectively.

Figure 7 shows the electrochemical behaviour of polyaniline and polyaniline containing 20 wt.% palladium nanoparticles. The cyclic voltammogram (CV) of the polyaniline film was characterised by the anodic peak near \(-0.5\) V, which is associated with the transformation from the LM to the EM state. The second redox peak of polyaniline corresponds to the redox interconversion of polyaniline from EM to PNA. The anodic peak (~ \(-0.5\) V) and cathodic peak (~ \(-0.8\) V) current of the polyaniline film containing the palladium nanoparticles gradually decreased with successive cycles. In addition, the composite film showed new anodic and cathodic peaks at about \(-0.1\) V and \(-0.3\) V, respectively. The redox peak of the polyaniline-palladium nanoparticle composite film shifted to the positive potential.

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![Fig. 6](image_url) AFM images of LM films: (a) after reaction with PdCl\(_2\); and (b) after reaction with Pd(NO\(_3\))\(_2\) for 10 min. \( R_a \) is the average roughness value. Reproduced from (16) with permission from the Royal Society of Chemistry.

![Fig. 7](image_url) Cyclic voltammograms of a polyaniline film: (a) without palladium nanoparticles, and (b) with palladium nanoparticles (20 wt.%) on the glassy carbon electrode in 0.1 M LiClO\(_4\)/propylene carbonate solution, measured at a scan rate of 20 mV s\(^{-1}\). Reproduced from (17) with permission from Elsevier.
region in comparison with the polyaniline film. This result implies the presence of strong electrochemical interactions between polyaniline and palladium nanoparticles. The complex formation process is readily evident in the CVs by the rapid growth of a pair of sharp redox waves at $E_{1/2} = -0.2$ V vs. Ag/Ag⁺ in the presence of palladium nanoparticles.

The interaction between polyaniline and the palladium nanoparticles was studied by UV-visible spectroscopic measurements (Figure 8). Palladium nanoparticles, which were stabilised and well dispersed in NMP solutions, showed a characteristic plasmon absorption at 280 nm (Figure 8(a)). The absorption peaks observed for polyaniline at 340 nm and 640 nm (Figure 8(g)) indicate that the polyaniline was partially oxidised. Adding the polyaniline to a palladium-NMP solution caused a blue shift of the peak near 640 nm resulting from the charge transfer from the benzenoid to the quinoid (Figures 8(b)–8(f)). The peak near 320 nm, which is due to the π-π* transition of the phenyl ring, also blue shifted. These spectral changes indicate that the coordination of the palladium particles to the nitrogen atoms permitted the palladium nanoparticles to interact with each other through the π-conjugate chain. Such a blue shift of the band at ~ 600 nm indicates the formation of a complex between the polyaniline and the palladium nanoparticles.

**Palladium and Polyaniline Derivative Composite Material**

The derivatives of polyaniline have attracted growing scientific attention since their chemical properties are similar to those of polyaniline. In comparison to the parent polymer, they exhibit better solubility in common organic solvents, which facilitates easier processing of these materials.

**Poly(3,5-dimethylaniline)-Palladium Nanofibre Composites**

For the preparation of polymer-palladium composite material an *in situ* synthesis approach is preferable. Since the polymer and the nanosized metal particles are produced simultaneously, this is expected to yield a highly intimate contact between the two components.

An *in situ* chemical synthesis route was used for the synthesis of a poly(3,5-dimethylaniline) nanofibre and palladium nanoparticle (polymer-metal) composite material in which the nanoparticles were highly dispersed in the polymer fibre matrix (18). Transmission electron microscopy (TEM) images (Figure 9) illustrate the composite material at different magnifications. Figure 9(a) shows an example of the large population of polymer fibres with different sizes, whereas Figure 9(b) images part of a single fibre, which is about 300 nm in diameter. The inset in Figure 9(b) shows the diffraction pattern from the fibre, revealing both diffuse scattering from the amorphous polymer and diffraction rings. Dark field imaging confirms that the rings originate from the palladium nanoparticles. Figures 9(c) and 9(d) show TEM images of the surface morphology and internal microstructure of the polymer. It is clear that the surface is not smooth. On both the rough surfaces and in the interior of the polymer, as shown by these and stereo pair images, there are highly distributed dark regions of diameter.
about 2 nm. Electron energy loss spectroscopy (EELS) mapping for the palladium distribution has confirmed that the dark spots are palladium. This is most clearly illustrated in Figure 10, which shows a fine strand of polymer composite, in which the particles were not overlapping. Figure 10(a) is a zero-loss image of the strand. This is an energy-filtered image; that is, it is derived only from electrons which have retained the energy of the beam when passing through the thin sample. The image therefore contains no analytical information. In contrast, Figure 10(b) is a palladium map from the same region. This palladium jump-ratio image was obtained by dividing the Pd-N₂,₃ post-edge loss image by the pre-edge loss image, thereby producing a signal derived from electrons that have lost energy by generating Pd-N shell X-rays.

**Palladium Nanoparticles in Poly(o-methoxyaniline)**

Metal-polymer composites with a nano- or micro-structured morphology have potential applications in various fields such as sensors, organic light-emitting diodes (OLEDs), field-effect transistors and nonlinear optics. A microstructured 3D rod-like morphology of a palladium-poly(o-methoxyaniline) composite material has recently been reported by our group (19). An *in situ* reaction between palladium acetate and o-methoxyaniline was employed. Figure 11(a) is a SEM image showing the product, which consists of regular straight nanofibres. An image at higher magnification, Figure 11(b), reveals the 3D structure of the nanofibres, which were up to about 15 µm in length, 0.5 µm in width and 0.25 µm thick. All the fibres were uniform in morphology and very straight, suggesting a high degree of rigidity. Raman spectroscopy was employed to determine the structural orientation of the polymer. As seen in Figure 12, the benzene C–H bending deformation mode lies at 1140 to 1190 cm⁻¹ for the reduced semiquinone and quinoid ring structure. The band at 1260 cm⁻¹ can be assigned to the C–N stretching mode of the polaronic units. The band at 1337 cm⁻¹ corresponds to the C–N⁺ stretching modes of the delocalised polaronic charge carriers, while the C–C stretching of the benzenoid ring was observed at 1600 cm⁻¹. A small peak positioned at 1460 cm⁻¹ cor-
responds to the C=N stretching mode of the quinoid units. A band of moderate intensity at 1500 cm\(^{-1}\) corresponds to the bending deformation of the N\(^•\)\(+\)–H unit.

A wide variety of methods have been applied to the preparation of polyaniline or substituted polyaniline type compounds by oxidative polymerisation of the monomer (20). We have suggested (19) that the mechanism for the polymerisation process involves the formation of a radical cation accompanied by the release of an electron, this being the initiation process for the polymerisation reaction. During the addition of palladium acetate, the pH of the reaction mixture solution dropped to ~ 5. Spectroscopic analysis confirmed that the –OCH\(_3\) substituted aniline oxidation product had only a head-to-tail (–N–Ph–N–Ph–) like arrangement rather than a head-to-head (–Ph–N=N–Ph–) type. The N–N characteristics arise from the head-to-head coupling only under neutral or basic pH conditions. On the other hand, aniline or substituted aniline oxidation products obtained in acid media have a predominantly head-to-tail arrangement (2).

The presence of the electron-donating group (–OCH\(_3\)) in the \(\alpha\)-methoxyaniline facilitates the relay of electrons through N\(^•\)–H\(_2\), which forms a covalent bond with Pd(II) and attains a species like [(OCH\(_3\))\_Ph–N\(^•\)–H\(_2\)]\(_\alpha\). Under acidic conditions, the [(OCH\(_3\))\_Ph–N\(^•\)–H\(_2\)] species undergo polymerisation (Figure 13), which is an oxidation process. Each step of polymerisation is associated with a release of an electron (21), leading to the reduction of Pd(II) to Pd(0). Subsequent coalescence of the atoms forms palladium clusters which are stabilised by the polymer. Figure 14(a) is a TEM image of this material revealing a uniform size distribution of palladium nanoparticles which are highly dispersed in the polymer matrix. A typical energy dispersive X-ray (EDX) spot analysis confirmed that dark regions in the polymer are palladium nanoparticles, Figure 14(b).

**Palladium Nanoparticles in Poly(\(\alpha\)-aminophenol) Needles**

Another example of an in situ chemical synthesis approach has been given by us (21) for the preparation of a palladium-poly(\(\alpha\)-aminophenol) composite material. Figure 15(a) shows a SEM image of the needle-like morphology of the composite material. TEM micrographs, Figures 15(b) and 15(c), indicate that the palladium nanoparticles are of the order of 2 nm in diameter and are highly dispersed within the polymer matrix. An IR spectroscopic study was used to determine the chemical structure of the polymer. In the IR spectrum, Figure 16, the characteristic band at 1588 cm\(^{-1}\) can be assigned to the C=C stretching of the quinoid rings, while the two peaks at 1499 cm\(^{-1}\) and 1470 cm\(^{-1}\) are the characteristic bands of the C=C stretching vibration mode for benzenoid rings.

**Palladium-Polyaniline Composite as a Sensor**

Athawale et al. (22) have shown that palladi-
um-polyaniline can be used as a methanol sensor. The nanocomposite material was synthesised by using a thermal reflux method followed by the oxidative polymerisation of aniline by ammonium persulfate, Figure 17. The synthesised nanocomposite was exposed to different aliphatic alcohol vapours such as methanol, ethanol and isopropanol. The results showed that the nanocomposite was highly selective and sensitive to methanol vapours. The sensor responded rapidly and reversibly in the presence of different concentrations of methanol vapour. The selectivity of the nanocomposite was further investigated by exposing it to mixtures of methanol–ethanol and methanol–isopropanol. Except for the response time, the nanocomposite was found to exhibit
an exactly identical response to that for pure methanol. The palladium-polyaniline nanocomposite was quite stable and showed no effects of ageing after exposure to different concentrations of methanol.

**Catalytic Activity for the Hydrogenation of Nitrobenzene**

The catalytic activities of palladium-containing electroactive polymer microparticles, typically 1.5 \( \mu \)m diameter, in the reduction of nitrobenzene to aniline have been studied by Huang and coworkers (23). Polyaniline was synthesised by adding ammonium persulfate to hydrochloric acid with vigorous stirring for 16 h. The resultant solid particles were then washed with excess hydrochloric acid and dried under reduced pressure. Polyaniline-SiO\(_2\) microparticles were also synthesised at ambient temperature by adding colloidal silica to a solution of ammonium persulfate in hydrochloric acid with constant stirring. Aniline was then added and the solution stirred vigorously for 16 h. The colloidal suspension was then centrifuged twice and stored in 1 M HCl until used.

The oxidation state of the resultant polyaniline and polyaniline-SiO\(_2\) was that of the emeraldine form (EM and EM-SiO\(_2\), respectively). The fully reduced forms of polyaniline, LM, and polyaniline-SiO\(_2\) (LM-SiO\(_2\)) were obtained after successive treatments with sodium hydroxide and hydrazine.

Palladium chloride was used as the precursor for incorporating palladium in EM, EM-SiO\(_2\), LM and LM-SiO\(_2\). Figure 18 shows the decrease in the concentration of palladium chloride as a function of reaction time. From Figure 18, it is apparent that LM and LM-SiO\(_2\) are more effective in uptaking palladium from the solution than either EM or EM-SiO\(_2\). It is also clear that SiO\(_2\) plays no direct role in the reaction with palladium.

The catalytic activity of the palladium-containing LM-SiO\(_2\) was tested for the hydrogenation of nitrobenzene and it was found that there was an almost complete conversion to aniline (Figure 19) after 2 h at 30ºC, whereas the catalytic activity of the LM without palladium in the hydrogenation of nitrobenzene was shown to be negligible.

Huang *et al.* concluded that the reactions are rapid when these electroactive polymers are
reduced to their lowest oxidation states. The electroactive polymers synthesised with SiO2 offer a larger specific surface area and a faster reaction rate for uptake reactions with palladium chloride than does the electroactive polymer without SiO2. XPS analysis confirmed that the palladium accumulation was in the form of Pd(II) rather than elemental metallic palladium.

Conclusion

Palladium-polyaniline and the derivatives of polyaniline composite materials are a very important addition to the repertoire of novel materials. From the standpoint of synthesis techniques, the morphology of these composite materials can be in various forms such as thin films, nanorods and nanofibres. The in situ chemical synthesis route is one of the most versatile approaches for the preparation of metal-polymer composite materials. By exploiting this approach, our group first reported a palladium-based polymeric hybrid material in which palladium nanoparticles of size ~ 3 nm were uniformly dispersed and encapsulated in the matrices of various derivatives of polyaniline. The matrices had a range of morphologies. Considering the progress of research in this field, it can be concluded that, in the near future, palladium-polyaniline composites will produce further significant advances in the field of materials science.

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Michael Witcomb has a Ph.D. degree from the University of Lancaster, U.K., and now is Director of the Electron Microscope Unit at the University of the Witwatersrand, where he holds a Personal Professorship. His current fields of research are the synthesis and characterisation of metal and metal alloy nanoparticle-polymer composites; precipitation processes in Pt-C and Pd-C alloys; phase diagram studies of intermetallic alloys; and microstructural characterisation of hardmetals.

Mike Scurrell has Ph.D. and D.Sc. degrees from the University of Nottingham, U.K., and is now Professor of Physical Chemistry at the University of the Witwatersrand. He has been fascinated by heterogeneous catalysis for the past 35 years and continues to focus on structure-activity relationships in this field. Special current interests are in catalysis by gold and other precious metals, activation and conversion of alkanes, and applications of spectroscopic techniques to further our understanding of surface chemistry and catalysis.
There are numerous platinum jewellery alloys available today. Two commercially available general purpose alloys that are in common use by manufacturing platinum jewellers are platinum-5% copper and platinum-5% ruthenium. In South Africa, the copper alloy is normally preferred for casting because of its lower melting point and greater fluidity, while the ruthenium alloy is preferred for hand-working and machining, although some jewellers use either alloy for all applications. In order to provide a scientific basis to the differences in finish and workability, as experienced by jewellers, we set out to compare casting characteristics of platinum-copper and platinum-ruthenium jewellery alloys and look for any substantial differences between them. We also examine factors affecting their different characteristics, and how working conditions can be manipulated to optimise the performance of each alloy in jewellery manufacture.

Many platinum jewellery alloys are available, each being marketed according to applications for which it is suitable. For instance, platinum-5 wt.% iridium has high work hardening and is suitable for making clasps, wire and the like, while softer platinum-5% palladium is used for fine casting and delicate settings (1). Two commercially available, general purpose alloys, platinum-5% copper (Pt-5%Cu) and platinum-5% ruthenium (Pt-5%Ru), are in common use by manufacturing platinum jewellers. Jewellers who work with these two alloys report some significant differences between them.

This paper will examine the differences in these alloys and reasons for their preferential use. We will look for factors affecting their different characteristics, and how working conditions can be manipulated to optimise the performance of each alloy in jewellery manufacture.

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<tr>
<th>Attribute</th>
<th>Pt-5%Cu</th>
<th>Pt-5%Ru</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness</td>
<td>Slightly softer</td>
<td>Slightly harder</td>
</tr>
<tr>
<td>Colour</td>
<td>Slightly brownish-grey</td>
<td>Shiny white</td>
</tr>
<tr>
<td>Melting temperature</td>
<td>Lower</td>
<td>Higher</td>
</tr>
<tr>
<td>Castability</td>
<td>More fluid</td>
<td>Less fluid</td>
</tr>
<tr>
<td>Surface finish</td>
<td>Susceptible to scratching</td>
<td>Easier to polish</td>
</tr>
<tr>
<td>Crucible corrosion</td>
<td>More corrosive</td>
<td>Less corrosive</td>
</tr>
<tr>
<td>Fuming when molten</td>
<td>Brown fumes</td>
<td>Minimal fuming</td>
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Physical Properties of Pt-5%Cu and Pt-5%Ru

The relevant physical properties of pure platinum, Pt-5%Cu and Pt-5%Ru are summarised in Table II. The alloys are formulated in terms of weight per cent (wt.%). Copper atoms are significantly lighter than ruthenium atoms. This means that the copper alloy contains a higher atomic per cent (number of atoms) than the ruthenium alloy.
There are 1.5 times more copper atoms than ruthenium atoms in an equivalent mass of 5 wt.% alloy. Both copper and ruthenium dissolve readily in platinum, and so do not decrease the density of the actual metal substantially.

In both the cast and annealed state Pt-5%Ru is slightly harder than annealed Pt-5%Cu. The addition of either of these alloying elements significantly increases the hardness of the platinum. The alloying atoms, acting like bollards on a busy pedestrian pavement, obstruct the movement of dislocations that allow planes of atoms in the metal crystals to slip past each other. This impediment makes the metal more resistant to deformation and increases the hardness. The bulk hardness is also affected by the microstructure, as will be seen later.

Pure platinum melts at 1769°C. Alloys can melt over a range of temperatures, depending upon their composition. As copper has a lower melting point (1083°C) than platinum, it lowers the melting range of the alloy (to 1725–1745°C). The much higher melting point of ruthenium (2314°C) raises the alloy melting range (to 1780–1795°C). Figure 1 clearly shows the narrower range of solidification at higher temperatures for Pt-Ru, compared to the broader range of solidification at lower temperatures for Pt-Cu. The different compositions of these alloys lead to substantial differences in their behaviour and melting temperature ranges, and these are described and explained here.

### Casting Experiments

A large number of casting tests were carried out in a Hot Platinum integrated induction melting and casting machine. This machine melts and casts up to 250 g of platinum alloy into a shallow cylindrical flask which is rotated around a vertical axis. The invested trees consist of a central sprue with the test pieces arranged tangentially. The test
pieces on each tree were two simple rings and two 10 × 10 grids, see Figure 2.

The testing was aimed primarily at assessing the fill and porosity that can be obtained when casting Pt-5%Cu and Pt-5%Ru in a number of different investment materials at different flask temperatures and centrifugal speeds. The investment materials used were Bego’s Wirovest, Ransom and Randolph’s Astro-Vest and Hoben’s Platincast. Duplicate tests were conducted mainly in pairs, under nominally identical conditions. Table III shows the test schedule. Results of a comparative metallographic study of rings from twenty five of these tests are reported here. An assessment of fill and porosity will be reported in a second paper.

Most of the twenty-five rings were sampled twice, by sawing through the line joining the feeder sprue to the ring shank and also perpendicularly through the shank at the distal point from the sprue. This produced two samples for each ring. These were mounted in resin, ground flat, diamond polished, and then electrolytically etched for examination by microscope in reflected light.

Results

Visual comparison of the etched metallographic sections revealed the following:

[1] Grain size varied considerably between samples, ranging from about 0.01 mm to over 1 mm, with the Pt-5%Cu tending to have larger grain size than the Pt-5%Ru under similar casting conditions. This gave rise to a measured 10% difference in the as-cast hardness.

[2] Within sample pairs for both alloys, the sprue sections always had coarser grains than the shank sections.

[3] All the etched Pt-5%Cu samples had a marked dendritic structure, while most of the etched Pt-5%Ru samples had an equiaxed grain structure without obvious dendrites, see Figure 3.

Chemical analysis of selected etched and unetched samples by energy dispersive spectroscopy (EDS) in a scanning electron microscope revealed the following:

[a] Analysis of unetched samples showed that the dendritic cores of the Pt-5%Cu were enriched in platinum, while the interdendritic areas were enriched in copper by about 1 wt.% (that is, about 20% variation relative to the bulk composition). This is evidence of strong chemical segregation.

[b] The aggressive electrolytic etching tended to dissolve the copper-rich interdendritic areas completely, producing strong visual contrast with the platinum-rich dendritic cores. The etching also leached copper from the platinum-rich cores. If the etched samples had been analysed alone, the segregation would have been visible but not detectable chemically.
Neither the unetched nor etched Pt-5%Ru alloy showed visible dendritic growth, but there was some compositional inhomogeneity within individual grains. Chemical analysis of an unetched sample revealed a maximum difference of about 0.5 wt.% Ru between platinum-rich and ruthenium-rich areas within individual grains.

**Discussion**

These results can be explained best with reference to the compositional or phase diagrams for these two alloys. A phase diagram is a plot of alloy composition against temperature and is useful, but not infallible, in predicting the state of an alloy under given heating or cooling conditions.

First let us consider how dendrites with strong compositional segregation form in the Pt-5%Cu alloy. Figure 4 shows part of the phase diagram for a platinum-copper alloy including our 5 wt.% composition.

The vertical axis represents temperature in °C and the horizontal axis represents alloy composition from 100% Pt on the left and increasing Cu towards the right. The Pt-5%Cu composition is

---

Table III

<table>
<thead>
<tr>
<th>Investment</th>
<th>Alloy</th>
<th>Melt, °C</th>
<th>Flask, °C</th>
<th>Centrifuge, rpm</th>
<th>No. of tests</th>
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<tr>
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<td>1000</td>
<td>4x</td>
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</table>
marked with a vertical dashed line. The upper line sloping down to the right is the liquidus, above which the metal should be fully molten. The lower line sloping down to the right is the solidus. Between these two lines we have a range of solidification, with solid metal coexisting with liquid. Below the solidus the material should be fully solid.

Let us consider what happens when we slowly cool a fully molten alloy with composition Pt-5%Cu through its solidification range. As the cooling liquid reaches the liquidus temperature, it does not freeze instantaneously, but solid begins to form. This solid has a composition corresponding to the solidus at this temperature, which is enriched in platinum. The liquid is thus enriched in copper. As the material cools further, more solid forms with a composition that tracks down the solidus. The residual liquid tracks down the liquidus, in composition. Under equilibrium conditions, that is, if the material cools slowly enough, there is a continuous reaction between the solid forming and the liquid, so that by the time the last vestige of liquid freezes all the solid has a uniform composition.

However, in reality cooling is usually too rapid for equilibrium to occur, and as solid forms it progressively removes the element with the higher melting point, in this case platinum, enriching the melt in copper. Because of the relatively wide solidification range of the Pt-5%Cu (from 1745–1725ºC) and the substantial difference in melting points of platinum and copper, there is opportunity during cooling for chemical segregation to occur. This accounts for the formation of dendritic crystals with platinum-rich cores and copper-rich margins.

Now, let us consider the cooling of a Pt-5%Ru alloy, with reference to the relevant part of the phase diagram, see Figure 5.

Ruthenium has a higher melting point than platinum, so on cooling a liquid Pt-5%Ru alloy the first
crystals to form at 1795°C should be ruthenium-rich, b, and the liquid will be enriched in platinum, a. On further cooling the solid composition should track down the solidus towards a more platinum-rich composition, bd. This explains the existence of ruthenium-rich cores to the crystals. The solidification range of Pt-5%Ru is narrower (1795–1780°C) in comparison with Pt-5%Cu, see Figure 1, and the cooling rate faster because of the greater difference between the temperature of the molten metal and the much cooler investment material. This means there is little opportunity for substantial segregation and cored dendritic growth to take place. The rapid solidification also explains why the equiaxed crystals in the Pt-5%Ru rings were much smaller than the large dendritic grains in the Pt-5%Cu.

In both cases, as the liquid freezes the first crystals to form are enriched in the higher melting point element. This enriches the liquid in the lower melting temperature element. Thus, for a short distance away from the freezing interface, the freezing point of the liquid is lowered below the actual temperature of the melt because of this compositional segregation. This constitutional undercooling is the mechanism that allows dendrites to grow from a freezing surface into a hotter liquid.

One way to suppress the dendritic growth, and produce a finer grained and more uniform
microstructure is to increase the thermal gradient or temperature difference between the freezing surface and the still molten metal (4). This can be achieved by selecting an alloy with a narrow solidification range, or by casting into a mould which is cool relative to the alloy’s melting temperature.

The fact that crystal size is influenced by the cooling rate, or thermal gradient, also explains why in all the paired ring samples studied the distal shank sections had finer grain size than the proximal sprue sections. The distal shank is surrounded by relatively cool investment material and freezes more rapidly than the sprue connection, which is in contact with the hot metal ‘reservoir’ of the sprue itself. Even if a lower metal casting temperature is used, there will be a difference in cooling rate of thicker and thinner sections, which is reflected in the eventual grain size.

Conclusions

The use of relevant phase diagrams coupled with metallurgical analysis of the microstructure can provide useful insight into the physical characteristics of jewellery alloys. However, using phase diagrams alone has limitations. They allow one to predict the compositions of phases present at equilibrium for different bulk alloy compositions and temperatures. To some extent they also enable the prediction of disequilibrium phase compositions, suggesting the possibilities for significant segregation on cooling, as observed for the Pt-5%Cu alloy, for instance. However, they do not allow prediction of the grain size, or the geometric relationships of grains to each other or to the margins of a casting. In order to evaluate the effects of grain size or grain orientation, microstructural analysis must be used, usually coupled with direct hardness measurements.

In practical terms, the finer and more uniform as-cast grain structure of Pt-5%Ru gives rise to about 10% greater indentation hardness. This in turn should contribute to easier polishing and enhanced scratch resistance, compared to the Pt-5%Cu alloy. We noticed no discernable difference in as-cast surface texture between the two alloys. It has been reported that Pt-Ru has a rougher as-cast finish (5, 6), but this may be dependent on the investment used. The main ingredient of most investments is silica, which melts at 1723°C. The higher melting temperatures required for Pt-Ru alloys could result in more reaction and pitting of the investment surface.

The wide solidification range of the Pt-5%Cu alloy gives rise to significant compositional segregation, with a 20% enrichment of copper to the interdendritic areas. This not only contributes to undesirable shrinkage porosity, but also imparts a brownish colour to the cast alloy because of the copper-rich areas.

From a microstructural point of view, it appears that if the higher melting temperature of the Pt-5%Ru alloy can be met, by induction melting for instance, then it is a superior alloy for casting. The greater uniformity in crystal size, shape and composition enhances both the colour and the hardness. The advantage of the greater fluidity and lower melting point of Pt-5%Cu is compromised by chemical segregation, leading to large dendritic crystals with compositional inhomogeneity, poor colour, and reduced hardness.

Acknowledgements

We thank Miranda Waldron of the Electron Microscope Unit at the University of Cape Town for assistance with the chemical analyses. The Centre for Materials Engineering at the University of Cape Town provided laboratory and office facilities. This research was funded by a grant from the Innovation Fund, administered by the South African National Research Foundation.

References

Reversible Gelation of Palladium-Based Fluid by Sound

Aggregating materials of low molecular weight by stimuli, electrochemically or with light, has been studied in gels, micelles, etc., to find ways to control fluidity, optical transmission, elasticity, and so on. Sound transmission increases molecular movement in liquids, but has not been considered suitable for molecular switching as it usually only breaks weak noncovalent interactions between molecules. Now, scientists in Japan (1) have developed the first molecule that is assembled by brief irradiation with ultrasound (sonication).

A dinuclear Pd complex, \( \text{I} \), stabilised by an intramolecular \( \pi \)-stacking, but inert to forming associations, can instantly become jelly-like in various organic solvents upon exposure to sound. A clear, homogeneous solution of \( \text{I} \) was prepared by the reaction of \( \text{Pd(OAc)}_2 \) with \( \text{N}_2\text{N}'\text{-bis(salicylidene)-1,5-alkanediamines} \) in boiling benzene (2). When placed in various solvents and irradiated with sound (0.45 W cm\(^{-2}\), 40 kHz) for a few seconds, the stable sol state was completely converted to gel. For instance, a \( 1.2 \times 10^{-2} \) M solution of \( \text{I} \) in acetone irradiated for 3 seconds at 293 K gave a totally opaque gel. Other organic solvents, such as \( \text{CCl}_4 \), 1,4-dioxane and ethyl acetate with \( \text{I} \) also gelled completely and instantly upon presonication for 10 seconds. However, without sonication these solutions remained stable at ambient temperature.

The resulting gels are readily converted back to the original solution by heating at above \( T_{\text{gel}} \), followed by cooling to room temperature. The controllable switching can be repeated indefinitely as the gel transition is due only to a simple conformation change of the complex. The aggregation rate can be controlled between ‘no gelation’ and ‘instant gelation’ by tuning the sonication time.

Conventional self-assembly depends on static reaction parameters, such as temperature, concentration, solvents and additives, but sonication gives dynamic control to the aggregation rate, so is a useful addition to chemistry — and possibly industry.

References


DOI: 10.1595/147106705X58961
In Part I of this paper, published here in July, we compared two commercially available casting alloys: platinum-5% copper (Pt-5%Cu) and platinum-5% ruthenium (Pt-5%Ru) used by manufacturing platinum jewellers (1). Optimised performance was obtained for each alloy by changes in their working conditions.

Testing precious metal jewellery alloys to evaluate the effects of casting variables is infrequent – due to the cost of the metal involved – so it is difficult to find explicit guidelines on casting. This is particularly true with platinum alloys which generally require specialised investment materials and high temperatures (2, 3), although alloys with reduced melting temperatures have been available for some time (4).

Testing the performance of a newly developed integrated induction melting and casting machine (Hot Platinum ICON3CS) provided an opportunity to study the effects of alloy composition on microstructure (1), and the effects of casting variables on fill and porosity. This paper reports the effects of varying flask temperature and centrifugal speed on the percentage fill of 10 x 10 grids and the porosity of 25 mm diameter rings, cast in two different platinum alloys using various investment materials.

In South Africa, the traditionally used alloy for casting platinum jewellery is Pt-5%Cu (melting range 1725–1745°C) because of its relatively low melting temperature and high fluidity compared to other commonly used alloys such as Pt-5%Ru (3). The performances of Pt-5%Cu and Pt-5%Ru (melting range 1780–1795°C) were compared. Pt-5%Ru is widely used for handworking, and the production of compatible cast components in the same alloy would be advantageous to match colour and hardness.

Our prior research showed that cast Pt-5%Ru is more homogeneous and has a finer grain structure than cast Pt-5%Cu (1). This current work shows that with the appropriate investment and rotational speeds good grid fill can be achieved with either alloy. Porosity is more difficult to control, because the casting process is inherently chaotic (5), but casting into a relatively cool mould minimises the probability of bad porosity for both alloys. Pt-5%Ru was found to be successful as a casting alloy when used with induction melting technology. It displayed superior uniformity, hardness and colour, compared with cast Pt-5%Cu alloy.

Casting Experiments

Casting tests were carried out in a Hot Platinum ICON3CS machine, which integrates induction melting and casting, see Figure 1. This machine...
routinely melts and casts up to 250 g of platinum alloy into a shallow cylindrical flask of radius 6 cm, which is rotated around a vertical axis. Rotational speeds from 350 to 1200 rpm are possible, generating accelerations equivalent to 8 to 97 G. It has a patented casting mechanism that ensures heat is applied to the metal throughout the melting and casting process, until the point at which the metal leaves the crucible.

The invested trees comprised a central sprue with the test pieces arranged tangentially. The test pieces on most trees were two simple rings 25 mm in diameter and two $10 \times 10$ grids, see Figure 2. These were combined for the sake of economy, but some tests were performed only with rings.

Testing was primarily concerned with assessing the performance of the machine, but provided the opportunity to study the percentage fill and porosity obtained when Pt-5%Cu and Pt-5%Ru were cast in different investments at different flask temperatures and centrifugal speeds. The investment materials used in the main test series were Bego’s Wirovest, Ransom and Randolph’s Astro-Vest, and Hoben’s Platinum cast. Most tests were duplicated under nominally identical conditions. Additional industrial trials on casting Pt-5%Ru were performed with Romanoff’s “J” Formula. The investment, burn-out, and devestment schedules are listed in Table I; test schedules and summarised experimental results are in Table II.

Results

The results of metallographic study of rings from twenty-five of these tests were presented earlier in this E-journal (1). Here we compare the performance of the four different investment materials and examine the effects of varying casting parameters, such as metal temperature, flask temperature, and centrifugal speed.

Investments

The investment process, summarised in Table I, closely followed the recommendations of the respective manufacturers in terms of volume of fluid to mass of powder. The burn-out cycles, see Table I, were arrived at after some preliminary experimentation, and in some cases differ slightly, but not substantially, from the recommended. The most obvious differences in the behaviour of the four investments were in their burn-out time and in the surface finish of the castings.

Wirovest provided the shortest burn-out, but the resulting castings had distinctly rougher surfaces than with the other investments. This is consistent with previously published results of casting platinum alloys in a quick burn-out dental investment (2). On the other hand, Wirovest was a strong investment which could be used to cast heavy thick sections and could withstand high rotational speeds without cracking. We used this investment to cast thick tubular sections in Pt-5%Ru, up to 350 g in mass, for the new South
African parliamentary mace. The investment manufacturer advised against water quenching. The consequent slow air cool made cleaning the hard investment from the castings difficult and it had to be removed mechanically by grinding. Wirovest is a dental investment which we would not recommend for general use by jewellers due to the rough surface finish, but it could be useful in specialist applications needing superior investment strength.

Astro-Vest and Platincast were largely similar in their working properties and burn-out times. The only noticeable differences were that Astro-Vest, which contains chopped glass fibre, had less tendency to crack during burn-out than Platincast, but Astro-Vest resulted in poor fill of most of the fine test grids (discussed in more detail below). Water quenching removed almost all the investment in both cases, except for a brittle glassy residue that formed in enclosed spaces in the castings with Platincast. This had to be removed mechanically. We would recommend either investment for general purpose jewellery production, with Astro-Vest having somewhat greater strength and Platincast aiding fill of thin sections.

The phosphate-based “J” Formula behaved very differently from the other investments. The investment slurry was thixotropic and the powder had to be added slowly to the liquid while stirring with a powerful mixer. The investment is designed not to set, but rather to congeal during the bench set, so instead of a rubber flask base a thick non-asbestos paper must be used and retained during burn-out. This leaves an ashy residue in the burn-out furnace, which could enter the casting mould. This investment was prone to cracking, with large-scale failure at high rotational speeds, and we failed to cast thick sections successfully with it. However, “J” Formula gave a very smooth surface finish and was indispensable for very fine castings, such as the 800 Pt-5%Ru beads, 2 mm diameter, cast for the new South African parliamentary mace. Cleaning up fine castings was simplified by the use of the proprietary “J” Break solution, a highly corrosive alkali requiring care in handling. Our experience

<table>
<thead>
<tr>
<th>Investment</th>
<th>Wirovest</th>
<th>Astro-Vest</th>
<th>Platincast</th>
<th>“J” Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>INVESTMENT</td>
<td>36 ml Bego “BegoSol” + water:powder (84 ml:800 g) mix, vacuum pour, vacuum bench set 2 h remove base</td>
<td>water:powder (218 ml:750 g) mix, vacuum pour, vacuum bench set 2 h remove base</td>
<td>water:powder (250 ml:750 g) mix, vacuum pour, vacuum bench set 2 h remove base</td>
<td>binder soln:powder (210 ml :700 g) mix, vacuum pour, vacuum bench set 2 h retain paper base</td>
</tr>
<tr>
<td>BURN-OUT</td>
<td>ramp 250°C, 1 h hold 250°C, 1 h ramp 570°C, 1 h hold 570°C, 1 h ramp 950°C, 1 h hold 950°C, 1 h</td>
<td>ramp 30°C, 0.5 h hold 30°C, 2 h ramp 150°C, 2 h hold 150°C, 4 h ramp 870°C, 6 h hold 870°C, 3 h</td>
<td>ramp 30°C, 0.5 h hold 30°C, 3 h ramp 150°C, 2 h hold 150°C, 2 h ramp 450°C, 2 h hold 450°C, 2 h ramp 900°C, 2 h hold 900°C, 2 h</td>
<td>ramp 30°C, 0.5 h hold 30°C, 1 h ramp 90°C, 1 h hold 90°C, 1 h ramp 180°C, 0.5 h hold 180°C, 1 h ramp 870°C, 2.5 h hold 870°C, 1 h</td>
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</table>
| DEVESTMENT | air cool manual clean | water quench manual clean | water quench manual clean | water quench clean with Romanoff “J” Break, platinum investment remover
indicates that "J" Formula is best used only for filigree castings, and at the lowest functional rotational velocities: to avoid investment failure.

**Fill Assessment**

All the rings filled completely, even at the lowest combinations of flask temperature and centrifugal speed. Fill was also assessed in tests with the 10 x 10 grids by counting the number of squares completely surrounded by metal. For each test this provided a pair of values, expressed as percentages (Table II).

The overall performances of Astro-Vest and Platincast were compared by calculating the mean grid fill for the two different alloys (Table III). The casting conditions for the Pt-5%Cu and Pt-5%Ru

### Table II

<table>
<thead>
<tr>
<th>Investment</th>
<th>Alloy</th>
<th>Melt, °C</th>
<th>Flask, °C</th>
<th>Speed, rpm</th>
<th>No.</th>
<th>Grid fill, %</th>
<th>Ring porosity</th>
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<td>870</td>
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<td>2x</td>
<td>77 &amp; 42</td>
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<td>Pt-5%Cu</td>
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<td>0 &amp; 59</td>
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<td>1200</td>
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<td>600</td>
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<td>72 &amp; 46</td>
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<td>97 &amp; 85</td>
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<td>94 &amp; 92</td>
<td>75 &amp; 41</td>
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<tr>
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<td>900</td>
<td>1000</td>
<td>2x</td>
<td>100 &amp; 100</td>
<td>100 &amp; 98</td>
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<td>600</td>
<td>600</td>
<td>2x</td>
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<td></td>
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<td>Pt-5%Ru</td>
<td>2000</td>
<td>900</td>
<td>1000</td>
<td>4x</td>
<td>rings only, with air bleeds</td>
<td>moderate to poor</td>
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<tr>
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<td>Pt-5%Ru</td>
<td>2050</td>
<td>900</td>
<td>1000</td>
<td>12x</td>
<td>rings only</td>
<td></td>
</tr>
</tbody>
</table>

\(n\) is the number of measured grids used to calculate the mean and standard deviations quoted for the replicate tests

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Porosity

Porosity was assessed by visual inspection of polished metallographic sections of cast rings. The standard test samples had two rings (see Figure 2), only one of which was sectioned. A section was cut through the base of the feeder where it connected to the ring (sprue section) and a transverse section was cut through the outer shank of the ring (shank section). These were mounted in resin and ground and diamond polished. A sub-sample of these was etched electrolytically and studied metallographically (1). The rest were photographed and the porosity assessed qualitatively in terms of ‘good’, that is acceptable, with either no porosity visible, or small pores away from the margins; or ‘bad’, that is unacceptable, with large pores or finer porosity near the margins of the casting (Table II). Typical examples are shown in Figures 7 and 8.

The melt temperatures were high in order to fill the grids cast with these rings.

We believe that most if not all of the porosity was gas porosity rather than shrinkage porosity, although with finer pores it is difficult to tell the difference. Inspection of the numerous photographs showed that porosity tended to be worse in the distal ring shank sections than in the sprue sections. This was surprising because the sprue sections had cooled more slowly than the distal shank sections, so were more coarse grained (1). Possibly, the proximity of the reservoir of molten metal in the thick feeder sprue had helped prevent the development of interdendritic shrinkage porosity in the slowly cooling sprue sections. It was also surprising that there was no obvious difference in the porosity of the two different alloys, given that generally the Pt-5%Cu had a coarser

### Table III

<table>
<thead>
<tr>
<th></th>
<th>Astro-Vest</th>
<th>Platincast</th>
<th>Platincast, without 6 duplicate tests at 800 rpm</th>
</tr>
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<tbody>
<tr>
<td>Pt-5%Cu</td>
<td>44.59 ± 30.76 n = 22</td>
<td>87.22 ± 24.23 n = 36</td>
<td>79.92 ± 27.92 n = 24</td>
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<tr>
<td>Pt-5%Ru</td>
<td>47.13 ± 31.58 n = 22</td>
<td>65.89 ± 36.16 n = 36</td>
<td>60.29 ± 38.94 n = 24</td>
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</tbody>
</table>

Casting conditions were broadly comparable for flask temperatures and centrifugal speeds. The difference in metal casting temperature of 200°C was to accommodate the higher melting temperature and somewhat lower fluidity of Pt-5%Ru.
grain size than the Pt-5%Ru under nominally comparable casting conditions (1). The lack of difference in porosity was evident by similarities in the ratios of good and bad porosity in both alloys in Astro-Vest and Platincast at comparable rotational speeds (Table II). Of the 58 comparable tests, Pt-5%Cu produced 13 good and 16 bad porosity results, while Pt-5%Ru produced 12 good and 17 bad. The almost identical ratios for this series of tests indicated that alloy composition had no discernable effect on porosity.

Nevertheless, a relationship was found between flask temperature and porosity. This is illustrated by a plot of the porosity index (the ratio of counts of bad to good porosity) for both alloys against flask temperature (Figure 9). There was a tendency to reduced porosity at flask temperatures between 600 and 800°C. Similar plots for the two alloys separately confirmed this trend for both alloys, with a minimum at ~ 600°C for Pt-5%Cu and at ~ 850°C for Pt-5%Ru. (The low numbers introduce more scatter, so only the combined ratios are illustrated.)

Cooling the flask to these temperatures before casting takes additional time, so we tried to reduce porosity at a flask temperature of 900ºC (the burn-out maximum), casting Pt-5%Ru at 1000 rpm into a Platincast mould with only four rings, but with added air bleeds to allow compressed gases to escape. Four tests were conducted and the porosity was moderate to poor in all the rings assessed under these conditions (Table II). Another 12 tests under similar conditions but without the air bleeds confirmed that high rotational speed alone, aimed at driving entrained gas into the investment, did not produce pore-free castings.

On the basis of these observations we would recommend that in order to minimise the porosity, after burn-out the flasks should be cooled to at least 1300°C below the temperature of the molten
platinum alloy before casting. This accords with
reports on a range of gold alloys, where lowered
flask temperatures were beneficial in casting alloys
had been heated significantly above their melting
points (5).

No relationship between porosity and rotation-
al speed was observed. Pairs of 'good' porosity
values were obtained at speeds of 600, 900 and
1000 rpm (Table II), while a plot of bad/good
porosity ratio against rotational speed showed no
discernable trend (Figure 10).

Discussion
Jewellery casting depends on the flow of metal
into a very convoluted mould at high speed to
avoid premature freezing. This is an intrinsically
chaotic process, and thus it is impossible to control
all the variables in such a way as to produce con-
sistently repeatable results. This is apparent, not
only from the tests reported here but also from
published results on other alloys (5). Nevertheless,
results can be optimised by operating within ranges
of casting parameters that minimise the statistical
probability of undesirable outcomes, like porosity.
There are not enough tests reported here for a rig-
orous statistical analysis, but some important and
useful trends are apparent and are described below.

There were significant and systematic differ-
ences in grain size between the cast Pt-5%Cu and
Pt-5%Ru alloys under nominally similar condi-
tions, with the Pt-5%Cu casts having much coarser
grains showing strong dendritic segregation (1).
This reduced the hardness and chemical homo-
geneity of the Pt-5%Cu castings. Impractical, long
annealing times would be necessary to homogenise
such dendritic segregations, and this would result
in grain growth and even larger grains, hence lower
hardness, as further undesirable results. Therefore,
the feasibility of using Pt-5%Ru for routine casting
was explored, despite its higher melting point and
lower fluidity than Pt-5%Cu.

The effects of casting variables on the percent-
age fill of fine grids and on ring porosity were
examined. Higher rotational speeds promoted
good fill, which was also affected by the choice of
investment material. Consistent with other studies
(2), porosity was always present, but there was a
tendency for porosity to be reduced by casting into
relatively cool flasks, at ∼600 to 700°C. The
choice of alloy appeared to have no effect on
porosity, although Pt-5%Ru produced consistently
finer grain size than Pt-5%Cu under nominally
similar casting conditions. There was no discernable relationship between centrifuge rotational speed and porosity, and having air bleeds seemed not to affect porosity in any consistent way.

Induction melting technology was used to overcome the difficulty of melting Pt-5%Ru quickly and economically. The problem of the metal solidifying on the cold lip of the crucible was avoided by continuing to feed power to the tilting induction coil while pouring took place. The lower fluidity of Pt-5%Ru, giving poor fill in filigree sections, can be compensated for by using a suitably strong investment and by increasing the metal melt temperature and rotational speed. This enables the jeweller to take advantage of the finer grain structure, superior hardness, and whiter colour of cast Pt-5%Ru, making cast elements compatible in terms of colour and fusing temperature with hand-worked elements in the same metal.

For general purpose casting, Platincast and Astro-Vest were easiest to work with and both produced good results. Platincast facilitated fill of thin sections, but Astro-Vest had greater strength, which could make it the investment of choice for bulky castings. The Wirovest dental investment, with the advantages of high strength and a very short burn-out cycle, produced a rough surface. Wirovest could be useful for bulky castings, but requires more finishing than the other investments tested. From our experience, we would recommend “J” Formula only for filigree castings at the lowest functional rotational velocities, although the “J” Break platinum investment remover made cleaning convoluted shapes easy.

Overall, for general casting of jewellery shapes, we would recommend Platincast investment and Pt-5%Ru alloy, cast in a flask cooled to 650ºC after burn-out, employing induction melting technology to cast at a metal temperature of 2000 to 2050ºC. The centrifugal speed would depend on the configuration of the centrifuge, as well as the size and shape of the casting, but should generate accelerations between 35 and 70 G.

Conclusions

Precious metal casting takes place at high temperature and centrifugal forces, and is intrinsically chaotic. Consequently, porosity in platinum alloy castings cannot be avoided altogether, but the probability of unacceptable porosity can be minimised. Casting into flasks at least 1300ºC cooler than the molten metal tends to reduce the occurrence of porosity. The behaviour of different commercial investments varies considerably and significantly in terms of strength and thermal conductivity. This means that the casting success rate can be increased by selecting the appropriate investment for particular tasks. High rotational speeds must be used in conjunction with a suitably strong investment material to obtain good fill in filigree sections. Induction melting and casting technology allows efficient melting of a higher melting temperature alloy, such as Pt-5%Ru, to take advantage of its superior colour, finer as-cast grain size, improved homogeneity, higher hardness and better polishing characteristics.
Acknowledgements

We thank Miranda Waldron of the Electron Microscope Unit at the University of Cape Town for assistance with the chemical analyses. The Centre for Materials Engineering at the University of Cape Town provided laboratory and office facilities. This research was funded by a grant from the Innovation Fund, administered by the South African National Research Foundation.

References


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Mechanical Properties Data for Pt-5 wt.% Cu and Pt-5 wt.% Ru Alloys

WORK PRESENTED AS A BASIS FOR FUTURE COMPARISONS

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Scant data exist for the mechanical properties of commercial platinum jewellery alloys Pt-5 wt.% Cu and Pt-5 wt.% Ru. Here data from new evaluations are presented on 90% cold worked and fully recrystallised heat treated alloys at 800°C. Recommendations are made for procedures in reporting future evaluations including disclosure of full processing details.

Platinum-5 wt.% copper (Pt-5% Cu) and platinum-5 wt.% ruthenium (Pt-5% Ru) are widely used alloys for platinum jewellery manufacture. It is therefore surprising that their mechanical properties are not well documented, as the mechanical properties of jewellery alloys are of fundamental importance in determining: (a) the ease with which the alloy may be formed into a jewellery item; and (b) the strength and durability of the finished item in service. Knowledge of mechanical properties is therefore beneficial to both jewellers and materials’ developers. Equally important is knowledge of the processing and microstructural condition of the alloy for which data are quoted, but even when mechanical property data are available, this information is often missing.

Some mechanical properties of pure platinum, Pt-5% Cu and Pt-5% Ru obtained from a review of available literature are shown in Table I. It can be seen that hardness values are well documented for most conditions, probably because determination of hardness involves a simple, non-destructive test which is quickly and easily carried out. However, while hardness testing is useful, it does not yield

<table>
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<th>Ultimate tensile strength, MPa at fracture</th>
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<td>30–40</td>
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<tr>
<td>Cold worked</td>
<td>100</td>
<td>234–241</td>
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<td>398</td>
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<td>90% cold worked</td>
<td>?</td>
<td>?</td>
<td>?</td>
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</table>

| Pt-5 wt.% Cu | | | | |
| As cast | 127 | 398 | 20 | 4 |
| Annealed | 110–120 | ? | 29 | 3, 5 |
| 50% cold worked | 215 | ? | ? | 5 |
| 90% cold worked | ? | ? | ? | |

| Pt-5 wt.% Ru | | | | |
| As cast | 127 | 456 | 25 | 4 |
| Annealed | 125–130 | 414–415 | 32–34 | 2, 3, 5 |
| 50% cold worked | 200–211 | 793 | ? | 2, 5 |
| Worked “hard”* | 210 | 795 | 2 | 3 |
| 90% cold worked | ? | ? | ? | |

* The amount of cold work is not specified in the reference; ? indicates no information is available.
easily interpreted results. Hardness is related to strength, ductility and elastic modulus, but these properties are not simply extracted from the hardness value. Conversely a properly conducted tensile test is easily interpreted, and the yield strength, tensile strength, elastic modulus and ductility can be more simply distinguished. For precious metals such as platinum, considerations of cost (tensile test specimens being relatively large) probably account for the paucity of tensile test data.

Table I also shows that most of the available information is for the annealed and as cast conditions, which are expected to exhibit similar values. With the exception of Lanam and Pozarnik (4), very few sources give processing information such as annealing temperature, or microstructural information, such as grain size. Also lacking are experimental details that allow other researchers to evaluate the data.

In order to test platinum jewellery alloys, a microsample tensile testing machine has been built at the University of Cape Town that can test samples of total length 8 mm. This paper reports on measurements of both the hardness and tensile properties of Pt-5% Cu and Pt-5% Ru, in the annealed and 90% cold worked conditions. The aim is to provide mechanical property values, averaged from multiple tests, from specimens for which detailed processing and microstructural information is provided.

Experimental Procedure

Although there is a pressing need to measure the mechanical properties of platinum alloys, it is not a very practical undertaking when the expense of the material is considered. Even the smallest specimens in the ASTM tensile testing standards (7) are beyond the means of many researchers. The approach used here: microsample tensile testing, has been used previously for other materials with success (8). It uses a very small sample that is as close to the ratios of the ASTM standard as possible while minimising the amount of material used. It is useful in this situation because it reduces the cost of carrying out multiple tests to provide adequate data. A schematic of the specimen design can be seen in Figure 1.

The specimen has a total length of 8 mm, with a nominal gauge width of 0.5 mm and a nominal gauge length of 2.26 mm. The thickness can be varied by the amount that the starting plate is rolled and is kept of the same order as the width. Typically the gauge width contains 5 to 10 grains but this is obviously determined by grain size.

The custom built apparatus is shown in Figure 2. A tensile specimen is positioned in the grips. The operation of the tensile testing apparatus is based on a screw driven actuator that applies a load to the specimen in the grips. Friction is reduced to a negligible amount with an air bearing. Load is measured with a 500 N load cell and displacement is measured with a miniature linear variable displacement transducer (LVDT) sensor. A computer records both displacement and load. Because displacement is not measured directly on the specimen, we do not regard the elastic strain data as reliable; furthermore analysis of the elastic response is complicated by elongation of the specimen ends in the grips. However, the recorded plastic elongation is reliable and compares well with direct measurements made on the specimens after testing. Examination of specimens after testing confirms that the plastic behaviour is concentrated in the gauge section.

To make the tensile specimens a plate is first rolled to the required thickness. If required, the plate is then annealed. This can take place before or after cutting. The cold worked specimens were cut with the tensile axis parallel to the rolling direction. The samples were cut using both a computer
numerical control (CNC) mill and wire electro discharge machining. The choice of cutting method was found to have little effect on the materials. The Pt-5% Cu and Pt-5% Ru samples were measured at two extremes of mechanical behaviour: the recrystallised and 90% cold rolled states.

Specific information about their processing is as follows: the as received material was homogenised first at 1000°C for 12 hours. It was then cold rolled to 90% reduction in thickness. Half of the material from each alloy was retained to perform testing of 90% cold rolled material. The remainder was heat treated at 800°C for six hours under vacuum. Light micrographs of the grain structure were taken. Hardness and tensile specimens were polished to a mirror finish for consistency. Small sample tensile tests and Vickers hardness tests with a 100 g load were performed with each set of specimens.

Results

Light micrographs from each set of material are shown in the figures. Figures 3 and 4 show the microstructure of the materials in the 90% cold rolled and 800°C heat treated conditions, respectively. As expected the 90% cold rolled material shows grains that are elongated in the direction of rolling. The heat treated Pt-5% Cu exhibits complete recrystallisation, with equiaxed grains of size ~ 100 μm. By comparison, the heat treated Pt-5% Ru alloy, Figure 4(b), shows finer grains, of size ~ 50 μm.

Figure 5 shows some typical tensile test results. As expected, the 90% cold rolled alloys exhibit a higher yield stress and significantly lower ductility than the recrystallised alloys.

The calculated average results of tensile tests are seen in Table II along with the hardness results.
It can be seen that the two alloys are not significantly different in strength, however, the Pt 5% Cu alloy is more ductile than the Pt 5% Ru alloy.

Discussion

If the new data in Table II is compared with the literature values quoted in Table I, it can be seen that the hardness and strength values obtained in the present work are consistently higher. This is expected for the cold rolled specimens, since the values obtained from the literature were for 50% cold worked alloys, and the results in the present work are for 90% cold work. The increased dislocation density in the 90% cold rolled specimens results in higher values for both hardness and strength, and very low ductility.

The difference in values for annealed specimens quoted in the literature and in the present work should also be evaluated on the basis of microstructure, but unfortunately heat treatment and microstructure data are not available for the values in the literature. The light micrographs in Figures 3 and 4 show that Pt-5% Ru has a finer grain structure than the Pt-5% Cu after heat treatment at 800°C. This suggests that the recrystallisation temperature of Pt-5% Cu is lower than that of Pt-5% Ru, consistent with the slightly lower melting temperature of Pt-5% Cu. The recrystallisation temperature for both materials is clearly 800°C or less after 90% cold work, and is certainly less than the 1000°C after an unspecified amount of prior cold work suggested in (3). The hardness and strength values in Table II show that the values for Pt-5% Ru are higher than for Pt-5% Cu.
Cu after the same heat treatment, which can be explained by the finer grain size of the Pt-5% Ru. Similarly, the difference in elongation may have more to do with the difference in grain size rather than real differences in the alloys. This illustrates the importance of both processing and microstructural information in evaluating mechanical property data.

The standard deviations of the strength data shown in Table II, illustrating the variation in values obtained in repeated tests of the same specimen type, are relatively large at around 10%. This underscores the necessity of carrying out multiple tests on each specimen type in order to obtain reliable average values for mechanical properties.

**Conclusion**

The results presented provide data to serve as a basis for comparison in further research on platinum alloys. It has been shown that the two most widely used platinum alloys are not significantly different in mechanical properties, and in addition, microstructure information and hardness values for each tested sample have been included. This is the most comprehensive information available on mechanical properties of these alloys and can serve as a baseline for alloy development. It is recommended that published mechanical data should include full processing information, microstructural characterisation if possible, number of specimens measured, and standard deviation or range of values obtained. This will greatly assist in evaluation of data and comparison with other measurements.

**References**

5. “An Introduction to Platinum”, Johnson Matthey, London, 1990, a manual of design and manufacturing processes, contact platinum@matthey.com

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Platinum Alloys for Shape Memory Applications

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Shape memory alloys (SMAs) are materials that can change their shape at a specific temperature and are used in applications as diverse as sensors, temperature sensitive switches, force actuators, fire-safety valves, orthodontic wires, fasteners, and couplers. The possible advantages offered by platinum-based SMAs involving the metals: iron, aluminium, gallium, titanium, chromium, and vanadium, are considered here and the likely systems upon which such alloys might be based are assessed. It is suggested that the most promising candidate systems are ternary-alloyed variations of the Pt₃Al and PtTi phases, although SMAs based on PtFe₁ have potential for low temperature applications. It appears possible to engineer a shape memory transition in the (Pt, Ni)Ti system anywhere between room temperature and 1000°C, a versatility which is probably unique among all known SMAs.

Metal alloys that can ‘remember’ their previous shape and return to it when required are known as shape memory alloys (SMAs). A ‘two-way SMA’ is one that can alternate repeatedly between two different shapes, whereas a ‘one-way SMA’ will change shape once and remain in that form. There are technological applications for both types of SMAs. Commercial SMAs based on nickel-titanium (Ni-Ti) or copper-aluminium-zinc (Cu-Al-Zn) were the first to be developed and gain popularity. However, these alloys can only be used up to ~ 100°C.

One of the interesting areas of application for SMAs is in the medical field in the form of in vivo implants, but neither Ni nor Cu is particularly biocompatible. In addition, there is interest in developing SMAs that can be used at higher temperatures for applications such as in jet engines, for example to switch or modulate fluid flows of various sorts as the temperature changes, using SMA-operated valves.

For these reasons, the authors embarked on a study of platinum-based (Pt-based) candidates for SMAs as it was anticipated that they might have both good biocompatibility and a wider temperature range of operation.

Shape Memory Displacive Transformations

In very broad terms, there are two types of phase transformation in the solid state. In the first, atoms diffuse and reposition themselves into a new phase in a relatively independent fashion, each individual atom moving randomly. In the other
type of transformation, whole rows of atoms shear or displace together, each atom moving in the same fashion as its neighbours, to produce a significant increment of the new phase in an instant. The latter type of solid state phase transformation is known as displacive. A displacive phase transformation in the alloy system is a prerequisite for SMA behaviour. However, displacive transformations have not been extensively studied in Pt-based systems.

This paper explores displacive transformations in some Pt systems and proposes systems that might have potential for future development as SMAs.

A variety of different definitions and classifications of displacive transformation exist, of which the martensitic transformation is a particular subclass (1). Martensitic transformations are defined in terms of their very particular crystallographic properties, and are considered to be the best basis for developing a shape memory effect. Delaey (1) proposed that they can be subdivided into three main types:

• allotropic,
• β-b.c.c. (body centred cubic) Hume Rothery and Ni-based SMAs, and
• α-f.c.c. → f.c.t. (α-face centred cubic to face centred tetragonal).

The allotropic option is not possible for Pt, leaving the transformation of the high temperature β-b.c.c. and the α-f.c.c. phases as the most likely for the development of Pt-based SMAs.

Displacive Transformations in Pt Alloys

Pt alloy systems that are known to undergo displacive transformations are described below. The transformations of each system will be examined.

Pt-Fe

One of the best documented martensitic transformations in Pt-based systems is that of PtFe. Pt-Fe alloys containing about 25 at.% Pt undergo an order-disorder transformation (2, 3). The disordered alloy has a f.c.c. structure and undergoes a martensitic transformation to a b.c.c. structure at around room temperature (4). Alloys containing more than 25.5 at.% Pt are also reported to transform martensitically from a disordered f.c.c. to a b.c.t. (body centred tetragonal) or alternatively to a f.c.t. structure, depending on composition.

Wayman (5) reported that no shape memory effect was observed in the disordered or partially ordered parent phases of PtFe, but that after ordering, the martensite transformation becomes thermoelastic, proceeding from f.c.c. to b.c.t. and back again, as many times as desired (6–8). Accompanying the increase in ordering is a drop in
the $M_s$ (the martensite start transformation temperature). It has been proposed by Muto et al. (4, 9) that the f.c.c. to b.c.t. and the f.c.c. to f.c.t. transformations are independent and competitive. The transformation temperature is very sensitive to changes in the composition and degree of order of the alloy. Oshima et al. (6) observed that the recoverable strain by the shape memory effect is small in the f.c.c. to f.c.t. transformation (< 3%). Larger strains would be more desirable in SMAs.

The 24 at.% Pt-Fe alloy is very hard and brittle, but ductility increases with increasing Pt content. The PtFe$_3$ system has some very interesting properties (such as a potential for magnetic-induced shape changes) and is worth exploring further. However, its $M_s$ temperatures are too low to meet the requirements of either a medical in vivo application or of a combustion engine. Therefore, it will not be considered here.

**Pt-Al, Pt-Ga**

A martensite-type transformation has been reported in both the Pt-Al and Pt-Ga systems. At around 75 at.% Pt, the intermetallic compounds Pt$_4$Al and Pt$_5$Ga undergo a phase change from $\gamma'$, a high temperature cubic ($L1_2$) structure, to $\gamma''$, a low temperature tetragonal ($DO_3$) structure, see Figure 1. Some workers (10, 11) have reported the existence of an intermediate phase, $\gamma'''$, ($DO_2$) although its existence is uncertain. The consecutive transformations of $\gamma' \rightarrow \gamma'' \rightarrow \gamma'''$ are reported to be martensitic in nature (10). The Pt-Al martensite phase transformation occurs in the region 73 to 78 at.% Pt, and $M_s$ is reported $\leq 1300^\circ$C (12), and between room temperature and 350$^\circ$C by others (10). For Pt-Al, at higher Pt contents, a Pt-rich solid solution exists which forms a eutectoid mixture with the tetragonal Pt$_3$Al phase. At least two, rather different, versions of the Pt-Al phase diagram have been published (10, 12).

**Pt-Ti, Ni-Ti, Pt-Ti-Ni**

A martensite transformation has been reported in the Pt-Ti system at around 50 at.% Pt. It is a displacive transformation from a cubic (B2) high temperature structure ($\beta$-TiPt) to an orthorhombic (B19) structure ($\alpha$-TiPt) at low temperatures, see Figure 2, and has an $M_s$ in the region of 1000$^\circ$C.

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**Fig. 2** For the Ti-Pt system, the crystal structure of parent and product TiPt phases (after Otsuka and Ren (13)). The parent is a B2 structure at high temperatures and transforms to an orthorhombic B19 structure at lower temperature. The $M_s$ temperature is $\sim 1000^\circ$C.
The cubic to orthorhombic transformation in this alloy is associated with a smaller temperature hysteresis than occurs, for example, for the cubic (B2) to monoclinic (B19') transformation in the well-known NiTi SMA (known as Nitinol), which has an Ms in the vicinity of room temperature (13). The Ms in PtTi is a maximum at 50 at.% Pt and decreases as the Pt content varies on either side. Although in NiTi the transformation would normally go from B2 to B19', it may, depending on alloy composition, do so via an intermediate rhombohedral (R) phase, or, if Pt is alloyed with the NiTi, via an orthorhombic (B19) phase. Depending on the composition, the reaction might not proceed any further, so the final product could be orthorhombic. Lindquist (14) has investigated the substitution of up to 30 at.% Pt for Ni in NiTi, and found that the alloys exhibited the one-way shape memory effect. An initial decrease in Ms was noted, but thereafter an increase in Ms, with increasing Pt content was reported. As a smaller temperature hysteresis is associated with the B2 to B19 transformation than the B2 to B19' transformation, this would affect the range of applications of a shape memory alloy.

**Pt-Cr**

Twinned microstructures have been observed in the 50 at.% Pt-Cr system by Waterstrat (15). The presence of twins could be due to a number of reasons: for instance, a displacive transformation, ordering, etc. Transformation from a disordered cubic structure to an ordered tetragonal structure occurs at ~1100°C, although dilatometry did not provide evidence for a displacive transformation (15).

**Pt-V**

The 50 at.% Pt-V alloy has an orthorhombic structure (B19) at room temperature (16), ostensibly transforming to a high temperature f.c.c. phase (based on the AuCu structure, that is, an ordered L10, f.c.c. structure) at ~1500°C (17). However, Waterstrat (16) who examined this system some 14 years earlier, did not record this. In fact, in most displacive transformations a low-temperature B19 phase is generally coupled with a high temperature B2 b.c.c. parent phase, which suggests that the nature of the high temperature phase in this system justifies another investigation. Twinning was observed, but it was concluded that, while this could have arisen from a martensite transformation, it was most likely to have been formed by an order-disorder transformation.

**Experimental Investigations**

**Screening Pt-X Binary Systems for Alloys**

Little further information, other than that mentioned above, has been published on Pt systems, and as there may be many other systems with the potential to be developed into SMAs, the authors screened the literature on binary Pt alloy systems, using the following criteria:

[1] The crystal structures of parent and product intermetallic phases were used as the primary discriminant. A displacive transformation implies that there is a crystallographic relationship between parent and product phase, and there are several known combinations of parent and product phase structures that satisfy this requirement. Sometimes information was available on only one phase, but if there seemed any possibility, based on the crystal structure, of a displacive transformation, the system was considered.

[2] The transformation temperatures were assessed as the second criterion. Only alloy systems likely to have an Ms above room temperature were studied further.

[3] The presence of twins or laths in the microstructure was the next criterion. While the presence of twins or laths does not prove that a martensite transformation has occurred (these features arise from a variety of phenomena, such as ordering), their absence was taken as an indication that a displacive transformation had probably not occurred. Again, this is not an infallible method, as twins or laths may be present, but may not have been exposed by the experimental technique utilised. For example, in the Pt-Al system it was essential to polish the samples with colloidal silica so as to image twins by scanning electron microscopy (SEM). The lack of twins was, however, used to eliminate systems and to narrow down the possible systems going for further investigation.

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The final criterion deemed important was ductility: only ductile alloys were selected. Hardness, while not always being a perfect guide to ductility, was used as an indicator (some alloys could be hard and yet still be sufficiently ductile). Alloys were also cold rolled to estimate the degree of ductility. Alloys that cracked on the first rolling pass were immediately eliminated from the study.

In order to decide whether a transformation is displacive, the relationship between the high-temperature parent phase and the product phase needs to be examined. This was often difficult as the parent phase was frequently only stable at exceedingly high temperatures, and more detailed work, including high temperature X-ray diffraction (XRD) and transmission electron microscopy (TEM), would need to be conducted before the true nature of a phase change could be determined. However, preliminary conclusions were made based on morphology and on the crystallographic relationships. At this stage, the aim of the investigation was merely to find some systems that might exhibit displacive transformations and that could have commercial application in the medical and high temperature fields.

**Sample Manufacture and Characterisation**

Alloy samples (1–3 g buttons) were prepared by arc-melting the individual elements into a button under an argon environment, on a water-cooled copper hearth. Buttons were melted three times to ensure mixing. In most instances, samples were first examined in the arc-melted state. They were subsequently solution treated to be wholly within the parent phase field, for periods of 3 days to a week, at 1200 or 1350°C for the Pt-Ti- and Pt-Al-based alloys, respectively, followed by furnace cooling. The alloys were then subjected to various further heat treatments.

Alloy hardness was evaluated on a Vickers hardness indenter with either 5 or 10 kg loads. At least six (and generally ten) indentations per sample per condition were performed, and an average is reported.

XRD data were gathered from the alloys, and the JCPDS database (the International Centre for Diffraction Data’s database of spectra of all known materials) (18) and Crystallographica (a software package) (19) were utilised in order to model lattices and predict the corresponding X-ray spectra. The modeling gave additional information regarding peak shapes as well as enabling the angular range to be extended beyond that of the JCPDS database thus allowing better comparison with the experimental data.

Samples were polished to a 0.25 μm finish, and some were further polished using colloidal silica. Samples were etched for varying times with a warm solution of 50% *aqua regia* (3:1 hydrochloric acid:nitric acid), 50% water. Examinations were performed by SEM. Elemental analysis was undertaken using energy dispersive X-ray spectroscopy (EDS) and pure element standards.

Differential thermal analysis (DTA), with scans taken in an argon atmosphere between 25 to 1500°C, was conducted at heating and cooling rates of ~5°C min⁻¹. Each sample was repeatedly cycled from room temperature up to 1200 or 1500°C if no melting was anticipated. Some samples also underwent differential scanning calorimetry (DSC) between 20 to 1395°C at a rate of 10°C min⁻².

Ternary phase diagrams ought to be based on quenched samples but due to experimental constraints this was not possible, so diagrams of the phases present after furnace cooling are presented. This has some merit as some of the final systems proposed here, either as possible SMAs or worthy of further study, would probably have to employ furnace cooling if commercialisation were to be considered.

**Alloy Screening Results**

Detailed results of the initial screening are reported elsewhere (20). Numerous Pt alloys were selected, based on the initial criteria, and then examined. Systems excluded from further study were:

- Pt-Fe: the transformation temperatures are below room temperature.
- Pt-Cu and Pt-Mn: both showed twins, but the results were not sufficiently encouraging or reproducible to merit investigation at this stage.
- Pt-Cr and Pt-V: both displayed twinning but the alloys cracked on the first pass of rolling.
However, the Pt-Al and the Pt-Ti systems both appeared to have the necessary prerequisites and were therefore studied in greater detail on their own, and with ternary additions of Ni and ruthenium (Ru). The results are discussed below.

Pt-Al

Samples containing 68 to 85 at.% Pt were studied. Arc-melted samples often had dendritic microstructures that were not completely removed by heat treatment. Samples of composition 68 to 73.9 at.% Pt contained the cubic Pt$_3$Al phase, while the arc-melted 68.8 at.% Pt sample also contained the Pt$_3$Al phase. There was no evidence of twinning in samples in this range (68 to 73.9 at.% Pt).

Samples containing 71 to 73.9 at.% Pt were all single phase (cubic Pt$_3$Al), while those in the 74.6 to 76.6 at.% Pt range contained a phase identified by XRD as the tetragonal Pt$_3$Al phase. This phase was twinned, as shown in Figure 3.

Samples in the 76.6 to 87.9 at.% Pt range comprised a eutectoid mixture of the tetragonal Pt$_3$Al phase and the Pt-rich solid solution phase. The eutectoid point was at about 80.6 at.% Pt. Twins were generally observed in the tetragonal Pt$_3$Al phase.

The high temperature phase fields were generally consistent with the phase diagram of Massalski (17). Attempts were made to measure the phase transformation temperatures and DSC proved to be more successful than DTA as the enthalpy changes were very small, resulting in very small peaks.

Mishima et al. (10) proposed that the phase field changed from (cubic Pt$_3$Al + (Pt)) to (tetragonal Pt$_3$Al + (Pt)) at ~340°C, whereas Massalski proposed that this change was at 1280°C (17). In fact, samples in the region 74.6 to 85.9 at.% Pt were found in this work to have transformations in the range 132 to 137°C, see Figure 4.

The transformation temperature was very sensitive to composition and, as the Pt content increased from 74.6 to 75.7 at.% Pt, the transformation temperature increased from 132 to 308°C. The 85.9 at.% Pt sample was a eutectoid mixture of Pt$_3$Al + (Pt) with a transformation temperature ~337°C. These transformation temperatures were more consistent with the phase diagram of Mishima et al. (10) than that of Massalski (17).

Fig. 4 Comparison of phase transformations detected in Pt$_3$Al by DSC and/or DTA in the present work, with those reported previously by Mishima et al. (10)
Hardness measurements were conducted to gain some idea of the mechanical properties. The measurements were found to depend on stoichiometry, varying between 350 to 650 HV<sub>10</sub>. Minimum hardness occurred at around 75 at.% Pt. However, the still relatively high hardness of the 75 at.% Pt alloy (350–400 HV<sub>10</sub>) suggested that the alloy might be difficult to work. Since all the other alloys were harder, it was felt that all the Pt-Al alloy range in this study might be difficult to work.

Nevertheless, limited amounts of cold rolling proved feasible, and the 75 at.% Pt alloy could be reduced by 18% (it hardened to 457 HV<sub>10</sub>) before cracking occurred. With appropriate thermomechanical treatment, our experience suggests that this alloy could be worked further. It was deduced that hot rolling could also be a possible processing route. While the Pt-Al transformation was martensitic in nature, the phase transformation was only observed in a narrow composition range and M<sub>s</sub> was exceedingly sensitive to the chemical composition of these button samples.

These features make Pt-Al an unlikely candidate for commercial application as a binary alloy. Ternary additions, using Ru or Ni, were then considered as a means to gain more control over the transformation by altering phase fields and stabilities.

**Pt-Al-Ru**

Ru was selected as a ternary alloying option as up to 40 at.% Ru dissolves in the Pt solid solution in the Pt-Ru system. A range of Pt-Al-Ru samples was investigated, containing between 5 and 20 at.% Ru, and a nominal Al content of 25 at.%. The intention was to substitute Ru for Pt in Pt<sub>3</sub>Al. The effect of Ru on the phase stability is best illustrated in a proposed isothermal section shown in Figure 5.

For low additions of Ru and high Pt, a mixture of Pt<sub>3</sub>Al and a Pt-rich solid solution (f.c.c.) containing Ru was observed. The Pt<sub>3</sub>Al matrix was generally twinned, see Figure 6, suggesting it was the tetragonal Pt<sub>3</sub>Al phase. In samples where the (Pt) phase was present in a Pt<sub>3</sub>Al matrix, heat treatment at 1350°C resulted in the (Pt) solid solution phase decomposing into smaller, very fine, spheres. This heat treatment also caused the Ru to
diffuse out of the matrix and into the Pt-rich solid solution. For larger additions of Ru, a mixture of cubic PtAl and a h.c.p. (hexagonal close packed) Ru-rich solid solution containing Pt was observed, see Figure 7. After heat treatment, there was minimal Ru dissolved in the PtAl matrix and minimal Al in the Ru-rich solid solution.

The hardness of all the samples was in the range 425 to 618 HV0.2 showing that adding Ru increased the hardness considerably. Also, the addition of at least 4 at.% Ru suppressed the cubic-to-tetragonal transformation of PtAl. For additions of less than 4 at.% Ru, a transformation temperature of about 350°C was indicated for the cubic-to-tetragonal change. The transformation temperature (at which the transformation occurred) was difficult to measure accurately because the enthalpy changes were very small.

The results suggest that the addition of Ru did not much extend the composition range of the parent PtAl phase. The appearance of cubic PtAl at room temperature in the samples with the higher Ru additions reflects that the tielines join h.c.p. (Ru) and cubic PtAl, rather than the tetragonal form. This means that there is at least one invariant reaction involving the terminal solid solutions, (Ru) and (Pt), and the two forms of PtAl.

Pt-Al-Ni

Nickel has been considered as a partial substitute for Pt (at least for non-medical applications) due to its similarity in metallurgical properties and its far lower cost. The region of present interest, in the Pt-Al-Ni ternary diagram (21), is dominated by the PtAl, tetragonal PtAl and (Ni, Pt) phases. However, there is an inconsistency between this ternary phase diagram and existing binary phase diagrams (10, 17) in that the ternary section does not show a cubic PtAl phase.

Heat treated samples in the Pt-rich end of the isothermal section, as well as samples containing only the PtAl phase were targeted, and the results are summarised in the proposed isothermal section at 1350°C for Pt-Al-Ni, see Figure 8. The...
samples in the Pt-rich end of the isothermal section, consisted of a mixture (eutectic or eutectoid) of Pt$_3$Al and (Pt). As the Pt content increased, the amount of the Pt$_3$Al phase diminished. The results show that there is a mixture of tetragonal Pt$_3$Al and (Pt) in the Pt-rich end of the Pt-Al-Ni section and a cubic Pt$_3$Al and (Pt) mixture at lower Pt contents. The tetragonal Pt$_3$Al phase underwent a displacive transformation. Nickel partitioned preferentially into the Pt-rich solid solution, but addition of Ni also extended the cubic Pt$_3$Al phase field into the ternary.

Many phases formed in the Pt-Al-Ni system (21). In addition to the Pt$_3$Al and Pt phases, a NiPt$_3$Al (Heusler phase) and a twinned phase (not Pt$_3$Al) were observed (20). The transformation temperatures were not detectable using either DTA or DSC. Hardness values ranged from 257 to 624 HV$_{10}$ depending on the phases present.

Pt-Ti

Samples of Pt-Ti containing 30 to 61 at.% Pt were examined. A two-phase region of Ti$_3$Pt and Ti$_3$Pt$_5$ (nominal stoichiometry) was observed between 30 and 43 at.% Pt, while between 43 and 46 at.% Pt, the Ti$_3$Pt$_5$ and TiPt phases coexisted. The TiPt phase has a wider stability range, unlike the other phases, and is stable between 46 and 55 at.% Pt. It occurs in a low temperature form (designated $\alpha$-TiPt) with B19 orthorhombic structure, and in a high temperature form above ~ 1000°C, ($\beta$-TiPt) with the B2 b.c.c. structure.

The $\beta$-TiPt structure cannot be preserved down to room temperature by quenching since it undergoes a martensitic transformation to $\alpha$-TiPt on cooling. The $\beta$-TiPt $\leftrightarrow$ $\alpha$-TiPt transformations are complex and, just like those in NiTi, take place via one or more intermediate structures (22). In the region 55 to 63 at.% Pt, both the TiPt and the Ti$_3$Pt$_5$ phases were observed. Further discussion on phase relations in the Pt-Ti system, including DTA studies which suggested complex phase relations, can be found elsewhere (20, 22).

The morphology of the $\alpha$-TiPt phase was dependent on the cooling rate. Figure 9 shows a typical lath-like structure observed in samples that were cooled rapidly. Figure 10 shows a finer twinned structure obtained after furnace cooling. The $\alpha$/$\beta$ transformation temperature for the TiPt
phase varied from 950 to 1050°C, and was a maximum at the stoichiometric composition and decreased on either side of it. The minimum hardness occurred at the stoichiometric composition. The slower cooled samples (furnace cooled) were softer than faster cooled samples (water quenched or arc-melted). A furnace-cooled 50 at.% Pt-Ti sample was the softest, with a hardness value of ~250 HV10, and could be cold rolled to ~50% reduction before cracking occurred. The sample was also hot rolled at ~1100°C to a reduction of ~90%, although oxidation was observed.

The stoichiometric TiPt composition appears to offer a good prospect for a workable high-temperature SMA, with a transformation temperature of ~1000°C. However, a means to reduce this temperature, and a better level of oxidation resistance, would be very helpful. For these reasons, the addition of ternary elements to Pt-Ti was then investigated.

**Pt-Ti-Ru**

The phase fields proposed for the heat-treated samples are given in Figure 11. The Pt-Ru system consists of terminal Pt-rich and Ru-rich solid solutions, and a two phase mixture in the region 62 to 80 at.% Ru. In the Ru-Ti system from 45 to 53 at.% Ru, a B2 TiRu phase is observed. The
terminal Ti-rich solid solution is h.c.c. at elevated temperatures, undergoing an allotropic transformation to h.c.p. on cooling.

Alloy samples investigated included ones in which Pt was fixed at 50 at.%, with Ru varying from 5 to 20 at.% Ru, as well as samples that were anticipated to be in phase fields surrounding TiRu or TiPt. Samples in the arc-melted state were generally cored and had to be heat treated at 1200°C for 3 days to obtain a reasonably homogeneous microstructure (23).

The addition of 5 to 10 at.% Ru led to a decrease in the TiPt transformation temperature (M, decreased from ~1000°C to ~700°C, while the hysteresis increased). The enthalpy change also decreased. These properties will affect the potential areas of application and determine whether small additions of Ru are desirable. For coupling applications, a large hysteresis would be desirable, whereas for actuator applications, a small hysteresis may be preferable.

The addition of Ru extended the TiPt phase field into the ternary diagram at least up to 19 at.% Ru. The results are summarised in a proposed partial isothermal section in Figure 11. The TiRu (B2) phase was noted to extend into the ternary up to about 15 at.% Pt. Thus, the two phases do not form a continuous field, despite sharing a common structure.

Pt-Ti-Ni

The addition of Ni to TiPt was also investigated for the same reasons as in the Pt-Al-Ni system. Nitinol (NiTi) is a well-known commercial SMA and some work has already been done on the substitution of Pt for Ni (24, 25). These studies concentrated on low additions of Pt (up to 30 at.%) and suggested that Pt-Ti-Ni alloys would show usable shape memory properties, but there were problems with formability (25).

The present work investigated a range of alloys and two rather different heat treatments. These were a homogenising heat treatment at 1200°C for 3 days followed by furnace cooling, and a solution anneal heat treatment at 1200°C for two hours followed by a water quench. The results are summarised in a proposed partial isothermal section in Figure 12. Nickel stabilised the α-TiPt extending it
Fig. 12 Proposed isothermal section for Pt-Ti-Ni at 1200°C (held at this temperature for 3 days followed by furnace cooling). Phase fields are indicated.

Fig. 13 The effect of Ni on the TiPt transformation temperature (reported and experimental). Some of the results of Lindquist and Wayman (25) are included for comparison.
temperature from nearly 1000°C to room temperature. The apparent lack of influence from Ni at low additions, and the variations in hardness observed in this range are more a consequence of slight variations in Pt and Ti content among the samples. At low Ni additions, the Pt and Ti content have a greater influence on transformation temperature (which is a maximum at about 50 at.% Pt), than the Ni content.

Another important issue to consider is which transformation is being monitored: B2 → B19 (TiPt) or the B2 → B19’ (TiNi). In this study, the B2 → B19 transformation was monitored. The samples containing Ni appeared to have lower enthalpy changes. There was no observed significant trend or change in hysteresis with Ni additions. The addition of 20.3 at.% Ni led to a M_s of 572°C and A_s (austenite start temperature) of 620°C which compared favourably to prior measurements of 626 and 619°C, respectively, for a 20 at.% Ni addition (25).

Hardness values varied from 226 to 626 HV_10 for alloys in the Pt-Ti-Ni system, depending on the phases present and on the heat treatment. For samples containing the α-TiPt phase, the addition of Ni generally increased the hardness. As in the binary study, the cooling rate significantly affected the hardness with the furnace cooled samples being the softest. The hardness was also affected by the Ti content; for example, a sample of 10 at.% Ni could have a hardness from 398 to 626 HV_10 as the Ti content varied around the stoichiometric point. The lowest hardness values were obtained at around 50 at.% Ti (the balance is Ni + Pt).

Comparisons of SMA Materials

The case for a commercial Pt-based SMA can only be advanced based on more specialised and unique technological property or properties of sufficient utility to overcome the initial cost of Pt. In the absence of such an incentive, it would make more sense to use the existing base-metal SMAs. However, it should be noted that most SMA applications are comparatively high-value in nature and they use rather small SMA components. Thus, the actual price differential between a Pt-based and a conventional component is not nearly as large as the differential in price of the raw material. Therefore, Pt-based SMAs may be acceptable for some applications.

As far as the existing base-metal SMAs are concerned, it is interesting to review briefly their shortcomings. Any Pt-based SMA that could solve one of these problems would have prospects for commercialisation.

Shortcoming of Current Base-Metal SMAs

- A first shortcoming of these materials is that they are comparatively brittle, and therefore expensive to convert into the desired form of wire or sheet. The lack of ductility follows directly on from their ordered, b.c.c. crystal structures. There is a fundamental lack of slip systems and dislocation mobility in such structures. Therefore, it is improbable that any Pt-based SMA, which as we have shown is also based on such alloy systems, would be fundamentally different. Nevertheless, reasonable ductility for TiPt has been indicated. This alloy seems to be at least as ductile as the best of current commercial SMAs, and thus it requires only some other technological advantage to make it a viable proposition.
- A second shortcoming of most commercial SMAs is that their working temperatures range from −150°C to −200°C. Neither of the common systems (NiTi or Cu-based) is able to function as a SMA at elevated temperatures. Furthermore, Cu-based systems have an intrinsic problem with ageing, and undergo an associated time-dependent change in properties. Therefore, they must be protected from exposure to temperatures much above 150°C. As we have seen, the Pt-based alloys offer the prospect of an enormous enhancement in operating temperatures, up to 1000°C. In a sense, this follows directly on from the far higher melting points of the parent compounds, although, other serendipitous factors such as the high temperature of the TiPt B2-to-B19 transformation also apply. A viable Pt-based SMA for elevated temperature application seems a very real possibility.
- Another issue with existing commercial SMAs is their corrosion resistance, or lack of it. These materials are obviously optimised for shape mem-

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ory effect and corrosion is very much a secondary consideration. Nitinol is reasonably corrosion resistant, but there appears to be some debate in the literature regarding its long-term biocompatibility (27, 28). There is no doubt that the Cu-based SMAs lack sufficient corrosion resistance for long term in vivo applications. These issues offer an opportunity for a Pt-based SMA, provided that it possesses sufficient corrosion and oxidation resistance for the given application. The high resistance of Pt to corrosion and oxidation is, in our experience, generally imparted in some measure to its alloys, which gives us a degree of optimism for possible medical application of Pt-based SMAs.

- Finally, another shortcoming of commercial SMAs is that the strain range over which they operate is quite limited, and thus working devices have to be designed to use changes in strain of the order of a few per cent. Any alloy that can show stable shape memory properties over greater strain ranges will have immediate applications. Regrettably, there is nothing to suggest to the authors that any such breakthrough would be achieved in a Pt-based composition.

It should be noted that SMAs operating above room temperature were targeted in this study, and this eliminated the FePt phase, which has a diverse range of interesting and technologically relevant properties.

The Pt-Al system at around 75 at.% Pt has a phase transformation which occurs from 132 to 337°C, depending on composition. This system is both corrosion resistant and capable of withstanding elevated temperatures. It exhibits superb oxidation resistance (29). However, the transformation is exceedingly sensitive to compositional changes which would make it a very difficult alloy to use commercially. Ternary additions of Ru did not appear to stabilise either parent or product phase. Nickel additions stabilised the parent phase (cubic PtAl) but promoted the formation of some Pt-Al-Ni phases which could complicate potential applications. On balance, while it appears possible to develop these materials as SMAs, they do not appear to be the best prospects.

The Pt-Ti system at around 50 at.% Pt has a displacive transformation from b.c.c. (B2) to orthorhombic (B19) at ~ 1000°C, which varied slightly with composition, but which did not appear to be a problem in terms of reproducibility. Figure 2 shows that this transformation occurs by a basal shear (111)[1̅1̅0] and a shuffle (13). DTA studies by the authors suggest that this transformation may be complex (20, 22). The 50 at.% Pt-Ti alloy could be cold rolled to 50% reduction, and was hot rolled to 90%, which showed it was workable. The alloy properties were strongly affected by heat treatment, with the cooling rate playing the biggest role. Slow cooling resulted in the softest alloys, with a finely twinned microstructure.

Ternary additions of Ni and Ru decreased the transformation temperatures to ~ 600 and 700°C, respectively, but increased the hardness. The main disadvantage of the Pt-Ti-based systems (besides cost) was the tendency for oxygen contamination and associated internal oxidation.

**Conclusions**

The most probable candidates from which to develop commercial Pt-based SMA systems are FePt, PtAl and TiPt. In each case, commercial alloys would also contain ternary or higher additions. The FePt alloys have working temperatures below room temperature, while both PtAl and TiPt have characteristics that suggest their use for in vivo and elevated temperature SMA applications.

The Pt-Al system (at around 75 at.% Pt) exhibits a displacive transformation from an ordered f.c.c. to ordered f.c.c. structure in the range 132 to 337°C. It appeared to be rather sensitive to compositional changes, and this might complicate its commercial application.

The Pt-Ti-based alloys (at around 50 at.% Pt) exhibit reproducible displacive transformations from b.c.c. (B2) to orthorhombic (B19) that have the potential for high temperature shape memory applications. Ternary additions of Ru and Ni, and possibly other elements, can be used to reduce the working temperatures to ambient, but this may be at the expense of a loss of ductility. These proposed systems can also be modified by control over their stoichiometry and thermomechanical processing.
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Searching at the European Patent Office

To find an indication of the intellectual property and commercial activity within any area, for example, shape memory alloys, the patents database, ‘esp@cenet’, of the European Patent Office: http://ep.espacenet.com/ is useful. The database offers a free quick search facility.

In the “Worldwide” database, around 30 millions past and present patent documents can be accessed, and can be searched with a combination of key words in the “Title or Abstract” section. This allows further, more complex, searching. Using the terms: shape memory platinum, located 20 patents in October.
Electrolytic Etching of Platinum-Aluminium Based Alloys

Enhanced microstructural analysis with improved safety using chloride solutions

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The microstructures of as-cast and annealed platinum alloys of different compositions were revealed after electrolytic etching in hydrochloric acid/sodium chloride solution using direct current. It was shown that the etching process enhances good microstructural images of platinum-aluminium based alloys.

1. Introduction
Etching of Pt-Al based alloys has been problematic because most of the alloys are designed to withstand oxidation and corrosion. Currently, binary Pt-Al alloys have been patented in the USA (1) as a catalyst for use in fuel cells. However, in this work higher order Pt-Al based alloys are being investigated as potential replacement for nickel-based superalloys used in high temperature and aggressive environments. The resistance to oxidation and corrosion is attributed to the formation of a protective Al oxide scale (2). Electrolytic etching can be considered as ‘forced corrosion’, where a previously polished specimen surface corrodes inhomogeneously, revealing the different microstructural features (3, 4).

Previously in South Africa (5–7), microstructural imaging of Pt-Al based alloys was done using scanning electron microscopy (SEM) in the backscattered electron mode. All the samples had been metallographically prepared by grinding using silicon carbide down to 1200 grit, diamond polishing down to 1 μm and finally polishing with oxide polishing system (OP-S, Struers A/S, Denmark) by which polishing is achieved through a combination of chemical treatment (the solution has a pH of 8) and gentle abrasive action. It allows selective polishing of softer phases thereby achieving a limited etching effect. Although some of the images derived from this method had reasonably good contrast, in some cases, the contrast was poor to the extent that analysis was rendered impossible. Figures 1–6 are examples of some of the images of Pt-Al based alloys taken using SEM in the backscattered electron mode. In alloy
Fig. 1. SEM-BSE of unetched, as-cast Pt$_{60}$:Al$_{2}$:Cr$_{38}$ (at%), showing cored single phase $\sim$CrPt and scratches (7).

Fig. 2. SEM-BSE image of unetched, as-cast Pt$_{63}$:Al$_{22}$:Cr$_{15}$ (at%), showing cored single phase $\sim$Pt$_3$Al (7).

Fig. 3. (a) SEM-BSE image of unetched, annealed Pt$_{81.5}$:Al$_{11.5}$:Cr$_{4.5}$:Ru$_{2.5}$ (at%), showing fine dark $\sim$Pt$_3$Al precipitates in light (Pt) matrix (6); (b) optical microscope image of annealed Pt$_{81.5}$:Al$_{11.5}$:Cr$_{4.5}$:Ru$_{2.5}$ (at%), after electrolytic etching in HCl/NaCl solution, showing fine dark $\sim$Pt$_3$Al precipitates in light (Pt) matrix more clearly.

Fig. 4. (a) SEM-BSE image of unetched, annealed Pt$_{78}$:Al$_{15.5}$:Cr$_{4.5}$:Ru$_{2}$ (at%), showing fine dark $\sim$Pt$_3$Al precipitates in light (Pt) matrix (6); (b) SEM-BSE image of etched, annealed Pt$_{78}$:Al$_{15.5}$:Cr$_{4.5}$:Ru$_{2}$ (at%), showing fine $\sim$Pt$_3$Al in light (Pt) matrix (6).
Pt₆₀:Al₂:Cr₃₈ (at%) (Figure 1), X-ray diffraction (XRD) analysis confirmed single phase ~CrPt (cored) and remnants of ~CrPt₃ from incomplete ordering. The poor contrast in the image made it impossible to deduce the phases from the microstructure and plot of the energy dispersive X-ray (EDX) composition analysis. The same applied to alloy Pt₆₃:Al₂₂:Cr₁₅ (Figure 2) whose XRD analysis confirmed the microstructure as single phase ~Pt₃Al (cored). The other four alloys were electrolytically etched in HCl/NaCl solution and their microstructure in the unetched and etched conditions are discussed subsequently.

In Germany (8, 9), electrolytic etching of Pt-Al based alloys has been done in aqueous potassium cyanide (KCN) solution for microstructure investigation. However, there are serious health and safety concerns regarding the use of KCN and its use in South Africa is very restricted, especially in laboratories. Two images of Pt-Al based alloys etched electrolytically in aqueous KCN solution are shown in Figures 7 and 8. Heat treatment of as-cast samples by two-stage ageing (variant B) resulted in the formation of coarse γ matrix and γ’ regions in alloy Pt₇₇:Al₁₅:Cr₃:Ni₅ (at%) (Figure 7) (8). Spherical precipitates of γ’ in a γ matrix were observed in alloy Pt₃₀:Al₁₉:Cr₂:Ni₃ (at%) after solution heat treatment at 1450°C for 24 h and ageing at 1000°C for 120 h (Figure 8) (9).

Most electrolytic reagents are simple in composition, being acidic, alkaline or salt solutions. The sample is nearly always the anode, although a few cathodic etching solutions have been developed (10). Direct current (DC) is mostly used, although a few solutions require alternating current (AC). In electrolytic etching, the process is controlled by varying the voltage and time (10).

Battaini (3, 4) obtained the best results for Pt alloys in saturated HCl/NaCl solution with an AC power supply when the voltage varied from 0.1 V to 10 V.
and the power supply provided a current of at least 10 A. Some of the electrolytic conditions are shown in Table I. However, the present work has shown that it is possible to get good results using a DC power supply.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 cm³ HCl (37%) + 10 g NaCl</td>
<td>Electrolytic, 3–6 V AC</td>
</tr>
<tr>
<td>10 cm³ HCl + 90 cm³ H₂O + 1 g FeCl₃</td>
<td>Electrolytic, 3–6 V AC</td>
</tr>
</tbody>
</table>

3. Results and Discussion
The electron beam voltage used to obtain the SEM-backscattered electron (SEM-BSE) images was 20 kV. Figure 3(a) and Figure 4(a) are SEM-BSE images of alloys Pt₈₁.₅:Al₁₁.₅:Cr₄.₅:Ru₂.₅ (at%) and Pt₇₈:Al₁₅.₅:Cr₄.₅:Ru₂ (at%), while Figure 3(b) and Figure 4(b) are the optical microscope images of the same alloys after electrolytic etching in HCl/NaCl solution. Both alloys had very fine dark ~Pt₃Al precipitates in light (Pt) matrices, which were difficult to discern from the SEM-BSE images. The contrast after etching is better and shows more clearly the dark ~Pt₃Al precipitates in the light (Pt) matrix, as well as the grain boundaries.

Figure 5(a) is a SEM-BSE image of alloy Pt₈₂:Al₁₂:Cr₄:Ru₂ (at%) which had a very poor contrast and after XRD analysis it was concluded that it had rounded dark ~Pt₃Al precipitates in light (Pt) matrix. After etching (Figure 5(b)), the optical microscope image showed a eutectic, as well as the dark ~Pt₃Al precipitates in light (Pt) matrix. Figure 6(a) is an example of an SEM-BSE image which had a reasonably good contrast and its optical microscope image after etching is shown in Figure 6(b).

4. Conclusions
There was a large improvement in contrast when the SEM-BSE images of alloys Pt₈₁.₅:Al₁₁.₅:Cr₄.₅:Ru₂.₅, Pt₇₈:Al₁₅.₅:Cr₄.₅:Ru₂, and Pt₈₂:Al₁₂:Cr₄:Ru₂ (at%) in the unetched conditions (Figures 3(a)–5(a)) were compared to the images of the same alloys (Figures 3(b)–5(b)) after being etched. Therefore,
electrolytic etching of Pt-Al based alloys in HCl/NaCl solution using direct current gives good results, and it is safer than using aqueous KCN solution.

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