A quarterly journal of research on the science and technology of the platinum group metals and developments in their application in industry

Virtual Issue 5 ‘The Platinum Decathlon’
August 2012

www.platinummetalsreview.com
Platinum Metals Review

A quarterly journal of research on the platinum group metals and developments in their application in industry
http://www.platinummetalsreview.com/

VIRTUAL ISSUE 5 ‘THE PLATINUM DECATHLON’ AUGUST 2012

Contents

Note: all page numbers are as originally published

Ten Application Areas and Ten Properties of Platinum or its Alloys

The Platinum Decathlon – A Tribute to the Foresight of Antoine Baumé
By Chris Barnard and Andrew Fones

1. Jewellery

Jewellery-Related Properties of Platinum
By John C. Wright

2. Biomedical Devices

A Healthy Future: Platinum in Medical Applications
By Alison Cowley and Brian Woodward
Original publication: Platinum Metals Rev., 2011, 55, (2), 98

3. High-Temperature Engineering

3.1 Glass Fibre Manufacture

The Manufacture of Continuous Glass Fibres
By K. L. Loewenstein
Original publication: Platinum Metals Rev., 1975, 19, (3), 82

3.2 Turbine Engines

The Protection of Gas Turbine Blades
By R. G. Wing and I. R. McGill

4. Ammonia Oxidation

The Ammonia Oxidation Process for Nitric Acid Manufacture
By L. B. Hunt

Compiled by the Editorial Team: Jonathan Butler (Publications Manager); Sara Coles (Assistant Editor); Ming Chung (Editorial Assistant); Keith White (Principal Information Scientist)
Platinum Metals Review, Johnson Matthey Plc, Orchard Road, Royston, Hertfordshire SG8 5HE, UK
Email: jmpmr@matthey.com

© 2012 Johnson Matthey
Contents (continued)

5. Sensors and Thermocouples

Lean-Burn Oxygen Sensor Material

6. Petrochemical Reforming

Platinum Catalysts in Petroleum Refining
By S. W. Curry
Original publication: Platinum Metals Rev., 1957, 1, (2), 38

7. Emissions Control

Opportunities for Platinum Group Metals in Future Emissions Control Technology
By Paul J. Millington and Andrew P. E. York

8. Hard Disks

Platinum in Next-Generation Materials for Data Storage
By Marge Ryan
Original publication: Platinum Metals Rev., 2010, 54, (4), 244

9. Silicone Manufacture

Platinum Catalysts Used in the Silicones Industry
By Larry N. Lewis, Judith Stein, Yan Gao, Robert E. Colborn and Gudrun Hutchins

10. Anticancer Drugs

Some Biological Effects of Platinum Compounds
By Barnett Rosenberg
Original publication: Platinum Metals Rev., 1971, 15, (2), 42
The Platinum Decathlon – A Tribute to the Foresight of Antoine Baумé

“So many excellent properties united in a single metal make it desirable that it should be introduced into commerce”, Antoine Baумé – “Chymie Experimentale et Raisonnée” (1773)

Introduction
Platinum (atomic number 78) is an element of the third row of the transition metal series and hence is one of the densest of metals (ca. 20 g cm⁻³) with a high melting point (>1750°C). It comprises only 1–10 ng g⁻¹ of the earth’s crust (1) making it a genuinely rare metal, with annual output less than a tenth that of gold. There are only a few locations in the world where platinum has sufficient concentration to make mining economically viable. The largest area of this type is the Bushveld igneous complex in South Africa, identified by Hans Merensky in 1924. In recent times this region has provided approximately three quarters of the world’s platinum supply.

The specific properties of platinum have been exploited over the years to create a range of consumer and industrial uses. These are indicated in Table I and below we will discuss how the applications have arisen.

Ten application areas and ten properties of platinum (or its alloys) are selected here to represent a “platinum decathlon”. Platinum has a unique combination of properties which make it eminently suitable for many applications from jewellery to anticancer drugs, from high-temperature engineering to a range of catalytic applications. The 18th century French chemist Antoine Baумé foresaw the desirability of platinum’s use in industry and its use today in many essential areas bears this out.

By Chris Barnard* and Andrew Fones**
Johnson Matthey Technology Centre, Blounts Court, Sonning Common, Reading RG4 9NH, UK
Email: *barnacf@matthey.com; **fonesar@matthey.com

http://dx.doi.org/10.1595/147106712X650811 http://www.platinummetalsreview.com/
Table I

<table>
<thead>
<tr>
<th>Properties</th>
<th>Value, units</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting point</td>
<td>~1770°C</td>
<td>✓</td>
</tr>
<tr>
<td>Ductility (tensile elongation, annealed, room temperature)</td>
<td>35–40%</td>
<td>✓</td>
</tr>
<tr>
<td>Oxidation resistance:</td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>1200°C</td>
<td>0.1–0.3 g m(^{-2}) h(^{-1})</td>
<td>✓</td>
</tr>
<tr>
<td>1600°C</td>
<td>1.2 g m(^{-2}) h(^{-1})</td>
<td>✓</td>
</tr>
<tr>
<td>Electrochemical oxidation potential</td>
<td>−1.2 V</td>
<td>✓</td>
</tr>
<tr>
<td>DC corrosion resistance</td>
<td>5–7 mg amp(^{-1}) year(^{-1})</td>
<td>✓</td>
</tr>
<tr>
<td>Relative radiopacity</td>
<td>30 × Ti</td>
<td>✓</td>
</tr>
<tr>
<td></td>
<td>6.7 × Ni</td>
<td>✓</td>
</tr>
<tr>
<td>Electrical conductivity</td>
<td>9.937 × 10(^6) S m(^{-1})</td>
<td>✓</td>
</tr>
<tr>
<td>Creep rate: 1000°C</td>
<td>0.04% h(^{-1})</td>
<td>✓</td>
</tr>
<tr>
<td>Coercivity: Pt/Co alloy</td>
<td>ca. 10 kOe</td>
<td>✓</td>
</tr>
<tr>
<td>Common oxidation states</td>
<td>0, +2, +4</td>
<td>✓</td>
</tr>
</tbody>
</table>

Ten Application Areas of Platinum

1. Jewellery

The values of rarity and purity, associated with its enduring quality and resistance to tarnishing, mean that platinum has been used for decoration since the 7th century BC, as shown by the Thebes casket (Figure 1). More recently, these qualities have made platinum a very popular metal for wedding rings (Figure 2) particularly in Asian countries and this has accounted for significant growth in platinum jewellery demand in China as consumer wealth has increased.

![Fig. 1. The Casket of Thebes](Image)
Each of the jewellery metals lends itself to particular types of work related to its properties. For example, pure gold can be used to provide large areas of reflective finish but it is too soft (Vickers hardness 25) for constructing many pieces and must necessarily be alloyed with other metals. Platinum is harder (Vickers hardness 45) but must still be alloyed with small amounts of other metals, which can include other platinum group metals, for jewellery use. Whereas platinum cannot be used for large areas of reflective finish, it is particularly suited to creating intricate designs using laser welding (2). The whiteness of platinum is also advantageous in not imparting any colour when setting stones, and it can be used to make very fine settings for holding stones which are not possible using gold.

A common jewellery component is wire. Platinum is formable enough that jewellery manufacturers can melt and cast small ingots before rolling them to rod and hand drawing to wire, allowing the wire to be produced as it is required (3). Platinum wire is a striking example of the ductility of platinum. The platinum can be drawn down to 0.0006 mm diameter for commercial supply. At that final thickness, if the wire was drawn down from a 10 cm long, 1 cm diameter rod, approximately 2777 km of wire could be produced.

2. Biomedical Devices

Biomedical devices are used inside a living body. There is a wide range of such devices, from the complex (pacemakers) (Figure 3) to the very simple (bone pins to help broken bones heal correctly), and even replacement parts (artificial knees or hip joints). All of these have a primary requirement that they do not harm the tissues exposed to them.

One problem suffered by in vivo devices is that they are exposed to the body’s naturally occurring fluids. The environment which these fluids form is not constant; for example, the pH can change with exertion. The fluids also contain a wide variety of ions, including chloride ions, which are known to be very aggressive in corrosion. As a result, biomaterials must be resistant to corrosion in a wide range of environments. If corrosion does occur it will result in metal ions being released into the body. These can be toxic to surrounding tissues, and will also interact with the fluids, potentially forming more dangerous compounds. Thus the corrosion resistance of platinum makes it a good candidate for biomaterials as it is not susceptible to this kind of reaction within the body. As a result platinum has been used increasingly as a biomaterial as the range of devices has been extended.

A given device will also have other properties required by its function. For example, one biomedical device with increasing use is the stent (Figure 4). Typically, this consists of a tube or scaffold and a balloon. The stent is inserted into an artery with the tube collapsed and carefully manoeuvred through the artery till it is in the correct position. The balloon is then inflated to expand the tube, then deflated and removed. The tube must be ductile enough to be opened, yet strong enough to remain open once the balloon is removed. It is also highly useful to the surgeon that the stent is radiopaque such that its position can be seen by X-rays to assist positioning. This can either be done through the use of marker rings if the stent itself is made of base metal alloy, or through construction of the stent using a platinum alloy, for example, chromium-platinum (37% iron, 33% platinum, 18% chromium etc.) as supplied by Boston Scientific. Since the first insertion of a stent into a patient in 1986 the design of stents has improved steadily. One problem which has been addressed for coronary stents is that of restenosis (4). This is the growth of smooth muscle cells at the site of the injury (analogous to a scar forming over...
an injury) leading to reblocking. Drug-eluting stents, where a drug is released from a biocompatible polymer forming the stent or a coating, can help in reducing restenosis (5). A temporary stent procedure can also be used to unblock arteries in the brain in people suffering strokes. A platinum-titanium stent (for example, as manufactured by Covidien) is guided to where the clot has formed and expanded to allow blood to reach the patient’s brain as soon as possible, minimising ischemic damage. The clot seeps into the mesh of the stent and after a few minutes the stent and clot are removed together (6).
A large number of other radiopaque platinum marker rings are also produced for other devices such as catheters to allow the surgeon to follow their progress during an operation.

The corrosion resistance and electrical conductivity of platinum have made it a metal of choice for the electrodes used in both pacemakers and neuromodulators, and the array of electrodes within a cochlear implant. A much older use is as a coating for irradiated iridium wire for localised delivery of radiation for cancer therapy. The tip of the iridium wire is left exposed, and the radiopaque platinum prevents the rest of the wire from affecting the body, allowing radiotherapy to be targeted on specific sites.

Platinum metal is therefore used for treating many conditions from deafness to Parkinson’s disease, to heart conditions, to cancer (7).

3. High-Temperature Engineering

3.1 Glass Fibre Manufacture

Glass fibres are produced by passing molten glass through a ‘bushing’ (8) (Figure 5). This consists of a box with many nozzles in the base. The glass strands produced from these nozzles are collected in a variety of ways depending on the planned application – for example the fibres may be broken by periodic blasts of cold air to produce fibres of a known length, or wound onto reels, or even allowed to settle into a tangled mat (used for fibre glass insulation). The driving force for improvements has been the desire to fit more nozzles into a bushing, requiring the nozzles to have the thinnest walls and be packed as tightly as possible. The application also exerts some high demands on the material. In order for the fibres produced from each nozzle to be the same, the force exerted on each nozzle by the molten glass must remain constant. The material used must therefore be able to retain strength, especially creep strength (avoiding deformation over long time periods under the influence of loads at high temperature) to avoid the base ‘bowing’. This results in the middle of the base sinking further than the edges, introducing a curve, and causing the nozzles to point in different directions, altering the forces at each nozzle. Stiffening ribs are often added to help mitigate this. The molten glass is also hot, alkaline and corrosive. The material must resist oxidation and chemical attack, both from the glass, and from impurities within the glass (for example, sulfur).

The materials used for this application are platinum-rhodium alloys. These have the strength at high temperatures and general corrosion resistance required by the application. Despite this, the bushings still only have a production life of approximately one year.

The requirement to fit more nozzles onto the base of a bushing has seen an increase in numbers from 51 in the original bushings to 4000 in more recent ones. This has been made possible by improvements in both processing and understanding (9). For example, the addition of rhodium improved the high-temperature properties, but also changed the way the glass wetted the nozzles. This made it possible to remove a countersink previously required to stop the glass flowing over the edges of the nozzle and coating the bushing, thus reducing the nozzle size. The nozzles can be made by either pressing and drilling out the ends, or by cutting holes in the base and welding on the nozzles. In both cases, the main limitation on how close to each other the nozzles can be is the space required for the processing equipment.

The ability of platinum-rhodium alloy to resist corrosion from the glass is also important in maintaining the purity of the glass. In recent years this has become important for the production of the liquid crystal flat screen displays which have become ubiquitous in mobile phones, computers and televisions.

3.2 Turbine Engines

Today’s civilian air fleet is propelled primarily by turbofan jet engines. A series of fans and compressors force air into the combustion chamber, where it is...
mixed with fuel and ignited. The gases expand and produce thrust to power the jet. The gas temperature rises as the gas is compressed throughout the engine, and the efficiency of the engine rises dependent on this gas temperature. As a result, the operating temperature of each stage has been increased over the years, and the materials used have therefore had to be improved to withstand higher and higher temperatures. The final compressor stage is now exposed to temperatures (1500ºC or more) which are above the melting point of the construction alloy used (a nickel-based superalloy) under highly oxidising conditions.

The blades need protection from these temperatures, and this is provided both by internal air cooling and by coatings to prevent the heat from reaching the blade. The coating must also protect the blade from oxidation. A platinum aluminide coating is a well-established technology to provide oxidation resistance (10) (Figure 6). Applying such a coating is a multi-stage process – first a platinum coating is applied (both aqueous and spray techniques are used for this) then the coated blade is heated to allow the platinum to diffuse into the nickel-based superalloy blade. The blade is then pack aluminised, which diffuses aluminium into the surface, forming a platinum aluminide layer. The layer greatly improves the oxidation resistance of the blades. As it was formed by diffusing platinum and aluminium into the nickel superalloy, it is well adhered to the surface. The platinum aluminide surface also allows a further ceramic thermal barrier layer to be applied. This ceramic layer helps to protect the blade from the high temperatures, but without the platinum aluminide coating, it would not adhere to the superalloy. The platinum aluminide coating allows the blades to operate continuously for 20,000 hours, and can be stripped and replaced once per blade.

4. Ammonia Oxidation

A major use for platinum wire is in the production of gauzes for nitric acid production in the Ostwald process. This is the oxidation of anhydrous ammonia to nitrogen dioxide over platinum (today generally a 90/10 or 95/5 platinum-rhodium alloy) at high temperature and pressure. The nitrogen dioxide is then reacted with water to make nitric acid. The platinum is in the form of woven or knitted (Figure 7) gauze sheets, and several of these sheets are stacked into a pack.

The process is a mature technology, having been patented by Wilhelm Ostwald in 1902. It was based on an 1838 patent by Kuhlman on the oxidation of ammonia over platinum sponge, which was in turn based on a 1789 experiment by Milner who oxidised ammonia over manganese(IV) oxide. The first plant was built in 1906, producing 300 kg of nitric oxide per day. By 1908 this production had been increased tenfold. These initial plants used crimped and coiled platinum strips, but 1909 saw the first use of platinum gauzes. The process became much more popular in 1913 when the Haber process for the production of ammonia was developed, and the two technologies have been linked since then (11).
The conditions for the Ostwald process (a typical example is 300°C and 9 bar pressure) are very aggressive (12). It therefore requires a very corrosion and oxidation resistant material, which must also catalyse the oxidation. The platinum-rhodium alloy used fulfils these requirements, but even such a resistant material is slowly consumed. The gauzes suffer from oxidation and slow loss of platinum (it is believed that this comes from the formation of a volatile platinum oxide). As a result, the gauzes slowly become less efficient and need replacement. The used gauzes are refined to recycle the platinum and rhodium. A further gauze is fitted downstream in the processing to catch and assist recovery of the lost platinum. Advances in gauze and catalyst design have also been incorporated over the years, such as the addition of palladium to the packs to reduce platinum loss, and the use of knitted rather than woven gauzes to reduce production costs (13).

The Ostwald process is also a key part of the agricultural industry as it supplies the nitrates required for fertilisers.

5. Sensors and Thermocouples

Platinum is used for a wide range of sensor applications. These range from thermocouples to more modern applications such as oxygen sensors in car exhaust systems.

5.1 Oxygen Sensors

Oxygen sensors for car exhaust gas (lambda sensors) (Figure 8) are used to help run a gasoline engine more efficiently (14). The oxygen content is related to the amount of unburned fuel remaining in the engine. The sensor consists of a porous platinum coating on both the inside and the outside of a zirconia tube. The tube is closed at one end and placed in the exhaust stream. This exposes the outside to the exhaust and the inside remains exposed to normal air. The exhaust heats the zirconia tube, which becomes an ionic conductor. As the oxygen content in the atmosphere at each platinum sensor is different, there will be a potential difference between them. This difference is monitored, and changes are used to control the fuel flow through the engine to ensure that the gas/fuel mixture allows for complete combustion of the fuel (15).

5.2 Thermocouples

A thermocouple consists of two wires of different metals (Figure 9). When any metal is subjected to a thermal gradient it will generate a voltage (the Seebeck effect). If two dissimilar metals are joined together, a potential difference will exist between them. Using a third metal to complete the circuit allows this potential to be measured, and compared to the voltage generated at a known temperature. This then allows the temperature of the joint between the

---

Fig. 8. Oxygen sensors for car exhaust gas (lambda sensors) monitor oxygen levels in the exhaust gases and provide feedback to the electronic engine management system which controls the air to fuel ratio (Copyright © Robert Bosch GmbH)

Fig. 9. A thermocouple consists of two wires of different metals joined together at one end to enable the temperature of the joint between the two metals to be calculated
two metals to be calculated. Platinum and platinum-rhodium alloys are used for three high temperature standard grades of thermocouple (16). Grade B links a 30% rhodium-platinum wire with a 6% rhodium-platinum wire, and is used at temperatures up to 1800°C. Type R links a 13% rhodium-platinum alloy with pure platinum and is effective to 1600°C. Type S joins a 10% rhodium-platinum wire to pure platinum and is also used to 1600°C. Type S thermocouples are also used as the standard of calibration for the melting point of gold.

6. Petrochemical Reforming
The major uses of petroleum products, both as fuels (motor, aviation and heating) and petrochemicals (solvents, polymers and plastics) require low molecular weight hydrocarbons. However, naturally occurring deposits contain a significant amount of heavier compounds that are unsuitable for these applications. During the refining of crude oil these heavier materials must be converted to the valuable lighter fractions by cracking and reforming processes. Platinum catalysts, which were first introduced by Universal Oil Products (UOP Ltd) in 1949, play a key role in these reforming processes (17). The catalysts offer a combination of the hydrogen transfer properties of platinum with the acid catalysis provided by the alumina support treated with chloride. This allows the isomerisation of alkanes to cyclic and branched structures and an increase in aromatic content that improves the octane rating. Over the years, improvements to the catalysts have involved the addition of promoters such as tin or rhenium and the thrifting of the platinum loading (18). Nonetheless, despite the recovery of platinum from used catalysts, the increase in demand for fuels in the corresponding period has required the steady increase in the amount of platinum used in this way.

The ability of platinum to catalyse hydrogenation/dehydrogenation processes also plays a role in the production of alkenes for polymerisation. In particular, processes to exploit the increasing amounts of shale-derived gas are of current interest. The dehydrogenation of propane to propene, the monomer of polypropylene, is one such process. Dow Texas Operations have recently announced that a 750,000 metric tonnes per annum propene plant, will be operational from 2015 using platinum catalysts as part of Honeywell UOP’s Oleflex™ technology (Figure 10).

7. Emissions Control
The ability of platinum to promote the oxidation of coal gas was identified by Sir Humphry Davy in the very earliest days in the study of catalysis (1817). This ability to promote the oxidation of hydrocarbons and carbon monoxide, while also allowing the reduction of nitric oxides to nitrogen, underlies the modern application of platinum in automobile exhaust catalysts (three-way catalysts) (Figure 11). This has become the largest use of platinum in the present day. Since the introduction of the first catalysts in the 1970s, there has been continual improvement due to the use of different promoters and support materials, with thrifting of platinum levels and substitution with palladium. The complex chemistry of reactions required has resulted in complex formulations for the catalyst coatings, with the support materials in the form of a coating on ceramic also playing an important part. Continuing challenges are provided by the progressive tightening of legislative limits around the world. Examples include the need for better performance at low temperatures, such as those occurring at start up of the engine, and
better control of nitrous oxide, which is a powerful greenhouse gas (19).

In addition to gasoline engines, the technology has now been developed for diesel engines. The exhaust gas from diesel engines contains higher levels of oxygen and more particulate carbon (soot) than gasoline emissions so a different approach is required. Particulate matter is removed by a diesel particulate filter (DPF) which is periodically regenerated by a high temperature excursion. Hydrocarbons and carbon monoxide are oxidised with a diesel oxidation catalyst (DOC) while reduction of nitrogen oxides requires the addition of a reductant, usually ammonia formed from urea injected into the exhaust stream, and a selective reduction catalyst (SCR) (20). The legislation to control these pollutants has now been extended from light vehicles to heavy-duty trucks and is being increasingly introduced to stationary diesel engines. The geographical spread of regulation along with the tightening of limits in mature markets provides the demand for continued developments in this area.

8. Hard Disks

While for many applications it is the properties of the pure element that lead to the use of platinum, its alloys also show useful properties that have brought about significant applications. One such is the use of platinum-cobalt based alloys as magnetic recording media (21) (Figure 12). Nanoparticulate grains of these materials create small magnetic domains with high perpendicular anisotropy and high magnetic coercivity, i.e. they are ‘hard’ magnetic materials providing permanent magnets. This has led them to being chosen as the materials of choice for magnetic data storage devices such as hard disks. In maximising the efficiency of data storage, it is important that the magnetisation is not influenced by the magnetisation of neighbouring domains and other local fields (degrading the data). Therefore, high coercivity is necessary to allow domain size to be reduced. In addition, other techniques, such as perpendicular recording and the use of ruthenium interlayers providing ‘antiferromagnetically-coupled media’, have also allowed a reduction in domain size, leading to data capacity increasing by 50% per year or more. In the future, new modifications to the technology such as heat-assisted magnetic recording or patterned media will allow further increases to data levels of up to 100 terabits per square inch (22). With this potential it is unlikely that other data storage methods such as the use of semiconductor materials will match the economy of hard disks, allowing them to remain as the preferred mass market data storage devices for some time to come.

9. Silicone Manufacture

Despite the fact that platinum metal is relatively inert, once dissolved (using chloride media) it displays a rich variety of coordination chemistry leading to uses in catalysis and biomedical applications (23).

The availability of the d-orbitals of transition metals provides the opportunity for the formation of coordination bonds with a wide variety of donor
groups. The reactivity of the ligands themselves is then modified leading to the potential for the formation of new bonds. This leads to homogeneous catalysis processes where, in contrast to heterogeneous catalysis, every atom of the metal is capable of acting as a catalytic centre. This property of platinum is used in the preparation of a wide variety of silicone polymers by the reaction known as hydrosilation. Typical catalysts range from simple salts such as potassium hexachloroplatinate(IV) to complexes such as Karstedt catalyst, Figure 13. Alkenes are inserted into silane precursors, $R_nSiX_{(4-n)}$ (for example, $X = H$) see Figure 14 (24, 25).

Silicone polymers have widespread application as easy-release surfaces and coatings. The different catalysts in combination with inhibitors can be used to control the initiation of the polymerisation, assisting in achieving great control over the properties of the final polymer. The catalyst (a few parts per million) remains embedded in the polymer and so this one of the few areas of application where recycling of platinum does not occur.

10. Anticancer Drugs

As one of the heavier transition metals the exchange reactions of ligands bound to platinum are slow compared to many metals, but this is not always an undesirable feature. In order to influence the function of cells in the body, limited reactivity is required to allow distribution of the chemical within the body, and in many cases strong bonding to reactive sites is necessary to bring about therapeutic benefit. It is just these properties that have resulted in platinum giving rise to some of the most effective anticancer agents of modern times. The first in this series of compounds, cisplatin (Figure 15), is a remarkably simple compound first synthesised by Peyrone in 1844. However, it wasn’t until the late 1970s that cisplatin was licensed for cancer treatment. Since then it has had a major impact on the treatment of testicular and ovarian cancer and is used widely in combination with other chemotherapeutic agents and other treatment modalities to benefit cancer patients (26). Other platinum drugs that have been licensed include carboplatin and oxaliplatin (Figure 16), extending the use of platinum agents to a wider group of tumours (27).

Sustainability

The increasing demand for platinum in a wide range of applications, some of which we have illustrated above, has in recent times been met by increased mine output. However, due to its high value in scrap, platinum has always been recycled where possible, for example, nitric acid gauzes, glass fibre bushings and reforming catalysts. In recent years, networks have been established for the recycling of automotive emission catalysts and this is playing an ever increasing role in the global platinum market. With the growth in the use of exhaust catalysts in developing countries and applications to a wider variety of engines, this can only increase. Although economic mineral resources of platinum are limited, it is clear that the market mechanisms exist to maintain supplies of platinum that will allow its unique benefits to be widely exploited now and in the future.
References

17. S. W. Curry, Platinum Metals Rev., 1957, 1, (2), 38

Fig. 16. Platinum anticancer drugs
Useful Additional Information Sources
PGM Database: http://www.pgmdatabase.com/
Platinum Today: http://www.platinum.matthey.com/

The Authors
Chris Barnard is a Scientific Consultant in the Catalysts and Materials group at the Johnson Matthey Technology Centre, Sonning Common, UK, with interests in homogeneous catalysis employing the platinum group metals. He is also interested in the application of platinum compounds as cancer therapy.

Andrew Fones is a Research Scientist at the Johnson Matthey Technology Centre, UK, working in the Platinum Group Metals Applications group. He is a corrosion scientist with a materials background, interested in the effects of platinum group metals doping on alloys.
Jewellery-Related Properties of Platinum

LOW THERMAL DIFFUSIVITY PERMITS USE OF LASER WELDING FOR JEWELLERY MANUFACTURE

By John C. Wright

The performance of precious metal alloys can be usefully compared by the application of engineering design theory and heat flow properties on the small scale that is required for jewellery production. Some of the physical and mechanical properties of platinum jewellery alloys differ significantly from typical gold and silver alloys to require modifications in the processing techniques, but these properties may allow for stronger slender designs. The thermal diffusivity of platinum jewellery alloys is significantly lower than that of other precious metal jewellery alloys. This explains why laser welding is so efficient when used in making platinum jewellery and why it also allows most of the cold work hardening to be retained in components.

Few jewellery designers or manufacturers start with a design specification, outline a design, detail a materials specification and optimise the production ability – which is the usual procedure in the manufacture of engineering components. Critical engineering design not only integrates mechanical design (such as stress/strain behaviour) with the properties of the materials and their interaction with the production process, but also has to take into account how all these factors have to operate in an acceptable economic and environmental framework. Most of the worldwide jewellery industry takes a traditional view that depends on a relatively narrow range of processes and materials and favours batch processing rather than mass production.

By applying engineering design theory and heat flow physical properties on the small scale required for jewellery, the performances of precious metal alloys can be compared. For example, properties such as Young's modulus, elastic limit stress and work hardenability of platinum jewellery alloys are significantly higher than those of the other precious metal jewellery alloys. This combination of properties can explain the favourable 'dead-set' capability of platinum settings, that is, claws/
prongs and similar settings when pushed against gemstones tend to remain in position and show little ‘spring-back’.

The thermal diffusivities of the platinum alloys used for jewellery are significantly lower than those for gold and silver, which explains why laser welding is so efficient and also why it allows more of the cold work hardening of jewellery alloys to be retained in components.

Laser Welding of Jewellery

Laser machines for jewellery are compact, low-powered and safe, see Figure 1. They weld most alloys quickly, repeatably and precisely, but the efficiency of the laser process depends very much on the properties of the target material. The energy that is effectively used in the welding depends on the surface absorption of the target and is controlled by adjusting pulse intensity, duration and pulse frequency. The laser welding effectiveness depends on properties of absorption, reflection and any chemical reactions of the target material. Components to be joined, or upgraded (repaired) in the case of castings, are arranged under visual control or jigged, and exposed to one or more laser pulses. A stereomicroscope and cross hairs facilitate the positioning of the parts and help to target the exact position where the laser pulse will strike.

The laser welding machine is easier to use if the shape of the beam in the working zone is cylindrical; this is because the spot diameter does not change over a range of focus of several millimetres, see Figure 2. A typical laser pulse lasts from 1 to 20 milliseconds and suitable adjustments can be made for various materials through trial and error, but certain heat flow data allow good predictions of suitable welding parameters. Material properties which need to be taken into account when welding jewellery alloys, including latent heats of melting and corresponding thermal conductivities, are available but these values are more accurately known at or near room temperature than around the melting point. Despite the high energy needed to melt platinum alloys, their relatively low thermal

---

Table 1
Typical Parameters of Jewellery Laser Welding Machines

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Machine size, height x width x depth</td>
<td>700–1350 x 250–550 x 650–860 mm</td>
</tr>
<tr>
<td>Weight</td>
<td>85–150 kg</td>
</tr>
<tr>
<td>Input power supply</td>
<td>115 or 200–240 V, 50–60 Hz</td>
</tr>
<tr>
<td>Max average operating power</td>
<td>30–80 W*</td>
</tr>
<tr>
<td>Focal spot diameter</td>
<td>0.2–2.0 mm</td>
</tr>
<tr>
<td>Pulse energy</td>
<td>0.05–80 J (W s)</td>
</tr>
<tr>
<td>Peak pulse power</td>
<td>4.5–10 kW</td>
</tr>
<tr>
<td>Pulse duration</td>
<td>0.5–20 ms</td>
</tr>
<tr>
<td>Pulse frequency</td>
<td>single to 10 Hz</td>
</tr>
<tr>
<td>Pulse energising voltage</td>
<td>200–400 V**</td>
</tr>
</tbody>
</table>

* Average light bulb power but in-phase, so equivalent to much higher power density.
** Voltage used to trigger xenon flash, in turn, affects laser beam output power.

---

![Fig. 2 A good quality laser beam is one where the beam shape in the working area is cylindrical so that the spot diameter is constant over several millimetres of focus.](image-url)
Table II
Typical Laser Welding Parameters For Some Jewellery Materials

<table>
<thead>
<tr>
<th>Alloy composition</th>
<th>Pulse energising voltage**, V</th>
<th>Pulse duration, ms</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Platinum, All</td>
<td>200-300</td>
<td>1.5-10</td>
<td>Very good welding results</td>
</tr>
<tr>
<td>Gold, 999 fine</td>
<td>300-400</td>
<td>10-20</td>
<td>Darken target area: high power necessary</td>
</tr>
<tr>
<td>Gold, 18 ct yellow</td>
<td>250-300</td>
<td>2.5-10</td>
<td>Good welding results</td>
</tr>
<tr>
<td>Gold, 18 ct white</td>
<td>250-280</td>
<td>1.7-5.0</td>
<td>Very good welding results</td>
</tr>
<tr>
<td>Silver, 925, 835</td>
<td>300-400</td>
<td>7.0-20</td>
<td>Darken target area: high power necessary</td>
</tr>
<tr>
<td>Titanium</td>
<td>200-300</td>
<td>2.0-4.0</td>
<td>Weld in inert gas inside the laser welding machine</td>
</tr>
<tr>
<td>Stainless steel</td>
<td>200-300</td>
<td>2.0-15</td>
<td>Weld in inert gas inside the laser welding machine</td>
</tr>
</tbody>
</table>

** Voltage used to trigger the xenon flash affects the output power of the laser beam used for the different materials.

Diffusivity allows the heat to be retained/concentrated at the target, so they can be efficiently welded. However, platinum jewellery alloys have casting temperatures around 2000°C and high solidification rates, so the challenge is for compact laser machines to achieve this.

The very high intensity laser pulse generates a surface temperature well above the melting point of platinum over a very small diameter target spot. This allows controlled welding, under ideal conditions, as close as 0.2 mm from complicated and heat-sensitive component parts, such as hinges, catches, fasteners, settings, most precious stones, and even, with care, pearls and organic materials. Provided that the heat flow away from the target is limited, it is possible to retain heat treated or cold worked hardness in most jewellery alloys; this works particularly well with platinum jewellery alloys.

The settings given in Table II are based on a beam diameter of about 0.5 mm on the materials stated and may need adjustment for other compositions. The main control settings on the laser machine (power/energy, beam diameter, duration) have slightly different effects on any one material, as shown in Figure 3. Different materials can have very different values for thermal diffusivity, melting temperatures and latent heats of melting. The way these properties combine together has a marked effect on the energy intensity needed to produce an effective weld. Welding is achieved only when adequate heat is absorbed through the surface, not when the beam is reflected off the surface, so surface colour and reflectivity have to be taken into consideration. Where there is a combination of high reflectivity and high heat dispersion (for instance in silver and high carat...
gold), it is helpful to mark and darken the target spot or line with a dark blue or black felt tip pen or permanent marker. This effectively increases the absorption coefficient of the surface.

**Why Platinum Responds Well**

The efficiency of a laser welding machine differs from alloy to alloy. While the same set of control parameters will result in the same power delivered in each welding pulse, the melting effect of each pulse depends on the proportion of the heat energy absorbed and then on the rate at which the heat is dissipated from the melting/welding zone. This is not simply a function of the thermal conductivity. Thermal conductivity is defined as the rate of heat transferred through a volume whose two extremes are at different but constant temperatures—a steady state. However, what matters more in dependable practical workshop technology, is how the heat is transferred from a hot-spot, such as where a welding torch touches a surface, through a mass whose temperature rises as a consequence, and thus where the 'low' temperature end is not at constant temperature. This property is best described by thermal diffusivity, still very dependent on conductivity but modified by the specific heat of the metal related to the volume:

\[
\text{Thermal diffusivity} = \frac{\text{thermal conductivity}}{\text{specific heat} \times \text{density}}
\]

The heat input parameters are:

[a] Specific heat of solid up to the melting point
[b] Melting (liquidus) temperature
[c] Latent heat of melting
[d] Specific heat of the superheated melt
[e] Thermal diffusivity

Melting points for most platinum alloys are high, but thermal diffusivities are relatively low (Table III) so the laser is able to deliver enough energy to melt a very small focused spot at each pulse but with only a small heat affected zone. With the possible exception of palladium, all the platinum group jewellery alloys respond in the same way to identical settings of a laser machine. Slight differences in surface colour when melting in air (alloys containing copper and cobalt tend to be a little greyer) have little effect on the optimum settings. Gold and silver alloys have lower melting points but five to seven times higher capacity to transmit heat away from the target.

The units used in Table II are c.g.s. units. This is because they fit the scale of jewellery alloys better than SI units (which rates thermal diffusivity in J m\(^{-2}\) s\(^{-1}\)) and the interest here is in the order of the effect rather than calculating the actual heat flow. The data for the pure metals are known most accurately around room temperature (2, 3) and data for the alloys were calculated from the properties of the pure metals, based on alloy composition by weight. The fullest version of the data was used where available. For instance, data for platinum, gold and silver have been more extensively studied than for, say, ruthenium. However, the data in Table III have been rationalised to two decimal places to give greater uniformity, while acknowledging that the accuracy at higher temperatures is questionable.

The laser beam does its most effective work at or near the melting point of the target metal so we should be more interested in data at and near melting point temperatures. Thermal conductivity increases with temperature for platinum from 0.171 at 300 K to 0.230 at 1800 K; and at the melting point it is around 0.24. Specific heat (more correctly, molar heat at constant pressure, \(C_p\)) within a single-phase region also increases with temperature according to a polynomial function:

\[
C_p = a + bT + cT^2 + dT^{1/2} + eT^3
\]

For platinum, \(a = 5.755, b = 0.001505, c = -0.185 \times 10^{-4}\), so the specific heat increases from 0.0316 at 273 K to 0.0452 at 2046 K.

Density decreases by the cube of the coefficient of linear expansion with temperature, which for platinum is 8.9 \(\times\) 10\(^{-6}\). This means that a cube of platinum, sides of 1 cm, at 273 K (21.40 g) would expand to a 1.016 cm sided cube at 2046 K, or volume 1.049 cm\(^3\), which is almost 5% less dense – at 20.04. On these assumptions, the thermal diffusivity of solid platinum at the melting point is approximately 0.265 instead of 0.245, about an 8% increase. All the platinum jewellery alloys have thermal diffusivities of the order of...
Table III
Melting Points and Thermal Diffusivities for Platinum Alloys and Other Jewellery Materials

<table>
<thead>
<tr>
<th>Metal/Alloy</th>
<th>Liquidus temperature, °C</th>
<th>Density, g cm⁻³</th>
<th>Thermal conductivity, cal (s °C cm)⁻¹</th>
<th>Latent heat, cal g⁻¹</th>
<th>Mean specific heat, cal g⁻¹ °C⁻¹ at 50°C</th>
<th>Thermal diffusivity, cm² s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>999 Platinum</td>
<td>1772</td>
<td>21.45</td>
<td>0.17</td>
<td>27.13</td>
<td>0.03</td>
<td>0.26</td>
</tr>
<tr>
<td>990 Platinum</td>
<td>1772</td>
<td>21.45</td>
<td>0.17</td>
<td>27.13</td>
<td>0.03</td>
<td>0.25</td>
</tr>
<tr>
<td>Copper</td>
<td>1684.5</td>
<td>8.93</td>
<td>0.96</td>
<td>48.90</td>
<td>0.09</td>
<td>1.17</td>
</tr>
<tr>
<td>Pt-5% Copper</td>
<td>1745</td>
<td>20.38</td>
<td>0.21</td>
<td>28.22</td>
<td>0.04</td>
<td>0.29</td>
</tr>
<tr>
<td>Cobalt</td>
<td>1794</td>
<td>8.80</td>
<td>0.12</td>
<td>63.00</td>
<td>0.10</td>
<td>0.13</td>
</tr>
<tr>
<td>Pt-5% Cobalt</td>
<td>1755</td>
<td>20.34</td>
<td>0.17</td>
<td>28.58</td>
<td>0.04</td>
<td>0.23</td>
</tr>
<tr>
<td>Iridium</td>
<td>2447</td>
<td>22.55</td>
<td>0.14</td>
<td>51.09</td>
<td>0.03</td>
<td>0.20</td>
</tr>
<tr>
<td>Pt-5% Iridium</td>
<td>1795</td>
<td>21.51</td>
<td>0.17</td>
<td>28.33</td>
<td>0.03</td>
<td>0.24</td>
</tr>
<tr>
<td>Pt-10% Iridium</td>
<td>1800</td>
<td>21.56</td>
<td>0.17</td>
<td>29.53</td>
<td>0.03</td>
<td>0.24</td>
</tr>
<tr>
<td>Pt-15% Iridium</td>
<td>1820</td>
<td>21.62</td>
<td>0.17</td>
<td>27.31</td>
<td>0.03</td>
<td>0.24</td>
</tr>
<tr>
<td>Pt-20% Iridium</td>
<td>1830</td>
<td>21.67</td>
<td>0.16</td>
<td>31.92</td>
<td>0.03</td>
<td>0.24</td>
</tr>
<tr>
<td>Palladium</td>
<td>1554</td>
<td>12.00</td>
<td>0.17</td>
<td>38.00</td>
<td>0.05</td>
<td>0.24</td>
</tr>
<tr>
<td>Pt-5% Palladium</td>
<td>1765</td>
<td>20.86</td>
<td>0.17</td>
<td>27.67</td>
<td>0.03</td>
<td>0.24</td>
</tr>
<tr>
<td>Pt-10% Palladium</td>
<td>1755</td>
<td>20.51</td>
<td>0.17</td>
<td>28.22</td>
<td>0.04</td>
<td>0.24</td>
</tr>
<tr>
<td>Pt-15% Palladium</td>
<td>1750</td>
<td>20.03</td>
<td>0.17</td>
<td>28.76</td>
<td>0.04</td>
<td>0.24</td>
</tr>
<tr>
<td>Rhodium</td>
<td>1963</td>
<td>12.42</td>
<td>0.21</td>
<td>53.00</td>
<td>0.06</td>
<td>0.29</td>
</tr>
<tr>
<td>Pt-5% Rhodium</td>
<td>1820</td>
<td>21.00</td>
<td>0.17</td>
<td>28.42</td>
<td>0.03</td>
<td>0.25</td>
</tr>
<tr>
<td>Ruthenium</td>
<td>2310</td>
<td>12.36</td>
<td>0.28</td>
<td>91.19</td>
<td>0.06</td>
<td>0.40</td>
</tr>
<tr>
<td>Pt-5% Ruthenium</td>
<td>1795</td>
<td>21.00</td>
<td>0.18</td>
<td>30.31</td>
<td>0.03</td>
<td>0.25</td>
</tr>
<tr>
<td>Tungsten</td>
<td>3387</td>
<td>15.25</td>
<td>0.35</td>
<td>61.00</td>
<td>0.03</td>
<td>0.34</td>
</tr>
<tr>
<td>Pt-5% Tungsten</td>
<td>1845</td>
<td>21.34</td>
<td>0.18</td>
<td>29.17</td>
<td>0.03</td>
<td>0.27</td>
</tr>
<tr>
<td>Fine Gold</td>
<td>1064.43</td>
<td>18.28</td>
<td>0.76</td>
<td>15.21</td>
<td>0.03</td>
<td>1.25</td>
</tr>
<tr>
<td>Fine Silver</td>
<td>961.93</td>
<td>10.50</td>
<td>1.02</td>
<td>25.00</td>
<td>0.06</td>
<td>1.74</td>
</tr>
<tr>
<td>Sterling Silver</td>
<td>893</td>
<td>10.40</td>
<td>1.00</td>
<td>26.40</td>
<td>0.06</td>
<td>1.68</td>
</tr>
</tbody>
</table>

0.23 to 0.27. A similar argument applied to silver, shows its thermal diffusivity decreases from 1.74 to 1.51 (near its melting point).

The heat energy contained within 1 cm³ cubes of liquid platinum, gold and silver at 100 K above their respective melting points, are 1854, 956, and 878 cal, respectively. Although the heat contents of molten platinum jewellery alloys are roughly double those of gold or silver, their thermal diffusivities are about one fifth of that for gold and one seventh of that of silver. So the rate of heat input to the target can still substantially exceed the rate of outward heat diffusion. In effect this means that the laser beam can be placed very close to delicate stones with platinum, and that normally it is unnecessary to remove stones before making repairs. A skilled operator can weld the surface without scarring and most components can be polished to 'near finish' before welding. Alternatively, components can be 'tack welded', adjusted to the correct position and final welds made with laser settings that improve the cosmetic finish of the tack welds.

Another feature of the localised heating effect of the laser is that dissimilar alloys can be joined more readily than when using bulk melting. There are incompatible pairs of metals, but a laser welding machine can produce narrow weld zones where the change in colour or texture between the two components is sharper and better delineated than in alternate technologies. The most obvious common feature of a typical range of laser welded platinum jewellery is that remarkably small sections,
Fig. 4 Platinum jewellery (not to scale) by Tom Rucker, who used laser welding in its assembly:

(a) A 16 ct beryl pendant (back view) made in platinum-5% copper. The beryl is held between 2 laser-welded rails. This design could only be achieved by laser welding.

(b) This diamond brooch made in platinum-20% iridium and 18 ct yellow gold was completely laser welded.

(c) Necklace with diamond brilliants, sapphires and pearls (2nd Prize, International Pearl Design Contest, Tokyo, 1999/2000) made in platinum-20% iridium and 18 ct yellow gold. The 0.6 mm diameter wire is assembled crosswise in two levels and laser welded.

(d) The "Sea of Lights" necklace made in platinum and 18 ct yellow gold with a 1.3 ct diamond brilliant. In the centre of the gold bowl is a brilliant cut diamond held in tension by 4 crossing platinum wires ~ 0.7 mm thick. The setting is so secure that brilliants up to 2 ct are used. The bowl is surrounded at the back by a cage of 0.4 mm platinum wire which also holds the bearing.

(e) A necklace with pearl clasp made in platinum-20% iridium. Platinum wire was wound onto the surface of a wooden ball and laser welded. The ball was then burnt away. The wire balls appear fragile, but the strong Pt-Ir alloy structure gives a solid result.
thin stampings and fine wire can be at least stitch welded with precision. More extensive welds and repairs of casting defects (see later section) can be made by a series of overlapping pulses. As the laser is limited to joints that can be hit by the direct beam, deep and undercut sites should be avoided.

Jewellery Design

Several components in the jewellery shown in Figure 4 have been elastically stressed to give springiness and rigidity. The tightly localised and limited heat diffusivity allows springy and hard components to be joined with little or no softening. This enables designs that make good use of lightweight springy sections or robust fasteners. The very limited heat affected zones also allow joining of more dissimilar alloys (assay rules permitting) than would be possible with large scale melting. In good commercial practice all the components could have a high degree of finish prior to joining. Most of the high finish is preserved, and it is clearly easier before welding to clean up and polish separate components than finished pieces.

Upgrading and Repairs

There are probably as many laser welding machines used for upgrading castings as there are for making welded pieces. Some surface defects can be repaired at the setting stage but small pinholes sometimes show up later during polishing. The expense to both the finisher and casser of returning such components for recasting is often avoidable by using the laser welder to upgrade the castings, particularly when casting and finishing operations are on the same site.

A small area of rough surface texture may be glossed by using a rapid repeat sequence of pulses with the laser beam set relatively wide and shallow. Small pinhole defects (around 0.25 mm) can be filled by similarly pulsing around the edge of the defect. Larger defects can be effectively filled with fine filler wire touched into the defect, cut to size with the laser beam striking the wire and then levelling the filler down to the original surface. The colour of the filler can usually be matched accurately to that of the casting. The principle of relatively low thermal diffusivities of platinum jewellery alloys when used with a laser machine, whether for upgrading castings or for welding, are virtually identical.

Conclusion

Comparing jewellery alloys, the necessary heat inputs to melt platinum alloys are high compared with gold and silver alloys, but thermal diffusivities are significantly lower. One effect is that heat is more localised around hot-spots than with gold and silver.

Most platinum jewellery alloys show the relatively high stress necessary to exceed the elastic limit, followed by a high rate of plastic work hardening which also raises the ‘bend-back’ stress. Components may have useful strength and springiness in slender sections, and these extra properties acquired before laser welding can be retained after assembly.

Acknowledgements

I gratefully acknowledge technical advice from Michael Buschek and David MacKellan of Rofin-Baasel UK Ltd., www.rofin.com. I am indebted to Tom Rucker of Anton Rucker, Ottostrasse 80, 65521, Offenbronn, Germany, who puts the technology expressed in this paper into very effective artistic design, and for permission to use several of his designs.

References

1. Rofin-Baasel UK Ltd., (formerly Basell LaserTech UK Ltd.), Drayton Fields, Daventry, NN11 5RB

The Author

John Wright is a former Professor of Industrial Metallurgy at the University of Aston in Birmingham. Currently, he is a consultant for the jewellery industry worldwide with Wilson-Wright Associates.

Laser Drilling of Platinum Cavities

A copper laser has been used to etch and bore into coated platinum wire electrodes (outer diameter 50–150 μm) to form ~ 30 μm diameter cavities for storing enzymes, by P. M. Vadgama of the University of Manchester (World Appl. 01/15,102). Cavities are formed in and along the length of the active electrode core. The enzymes face laterally, instead of being on a mechanically vulnerable tip, which improves effectiveness and ease of use. The electrodes are for in situ biological sensors.

Platinum Metall Rev., 2002, 46, (2)
A Healthy Future: Platinum in Medical Applications

Platinum group metals enhance the quality of life of the global population

The world’s growing population demands increasing access to advanced healthcare treatments. Platinum is used to make essential components for a range of medical devices, including pacemakers, implantable defibrillators, catheters, stents and neuromodulation devices. The properties of platinum which make it suitable for medical device applications include its biocompatibility, inertness within the body, durability, electrical conductivity and radiopacity. Components can be manufactured in a variety of forms, from rod, wire and ribbon to sheet and foil, plus high-precision micromachined parts. As well as biomedical device components, platinum also finds use in anticancer drugs such as cisplatin and carboplatin.

Introduction

According to the United Nations Environment Programme (UNEP), the global population will reach over 9 billion by 2050 with nearly 90% of the world’s people located in developing countries (Figure 1) [1]. Since the early 1970s, platinum has been used in a variety of medical devices for people around the world suffering from such ailments as heart disease, stroke, neurological disorders, chronic pain and other life threatening conditions. In 2010, some 175,000 oz of platinum are estimated to have been used in biomedical devices, of which around 80 per cent was for established technologies such as guidewires and cardiac rhythm devices. The remaining 20 per cent was used in newer technologies, such as neuromodulation devices and stents. In addition, over 25,000 oz of platinum are used annually in anticancer drugs [2].

With an ageing and increasing world population, there will be an increasing demand for healthcare products and services that use components made from platinum, other platinum group metals (pgms) and their alloys. Increasing access to healthcare and advanced medical treatments in developing countries means that platinum contributes to improving the quality of life of people around the world.
The Advantages of Platinum for Biomedical Uses

The chemical, physical and mechanical properties of platinum and its alloys make them uniquely suitable for a variety of medical applications. Agnew et al. (3) and Brummer et al. (4) carried out studies which confirmed the low corrosivity, high biocompatibility and good mechanical resistance of platinum and platinum alloys that are used for medical applications.

Platinum’s biocompatibility makes it ideal for temporary and permanent implantation in the body, a quality which is exploited in a variety of treatments. As a metal, it can be fabricated into very tiny, complex shapes and it has some important properties not shared by base metals. It is inert, so it does not corrode inside the body unlike metals such as nickel and copper, which can sometimes cause allergic reactions. Modern, minimally-invasive medical techniques often use electricity to diagnose and treat patients’ illnesses, and platinum’s conductivity makes it an ideal electrode material. It is also radiopaque, so it is clearly visible in X-ray images, enabling doctors to monitor the position of the device during treatment. Some examples of areas where pgms are used in medical devices, together with some of the manufacturers currently active in the medical device market, are shown in Table I.

For more than forty years platinum alloys have been employed extensively in treatments for coronary artery disease such as balloon angioplasty and stenting where inertness and visibility under X-ray are crucial. In the field of cardiac rhythm disorders, platinum’s durability, inertness and electrical conductivity make it the ideal electrode material for devices such as pacemakers, implantable defibrillators and electrophysiology catheters. More recently, its unique properties have been exploited in neuromodulation devices (including "brain pacemakers", used to treat some movement disorders, and cochlear implants, to restore hearing), and in coils and catheters for the treatment of brain aneurysms.

Platinum in Biomedical Applications

Devices for Cardiac Rhythm Management

Abnormalities of the heart’s rhythm are common, often debilitating, and sometimes fatal. For example, bradycardia is a condition in which the heart’s “natural pacemaker” is set too slow, resulting in fatigue, dizziness and fainting. Other patients may be at risk of sudden cardiac death, a condition in which the heart’s lower chambers (the ventricles) “fibrillate”, or pulse in a rapid and uncoordinated manner. This prevents the heart from pumping blood and leads rapidly to death unless the victim receives cardioversion (a strong electric shock to the heart, which restores normal rhythm).

These and other cardiac rhythm disorders can now be managed very successfully using implanted...
devices such as artificial pacemakers (5, 6) and implantable cardioverter defibrillators (ICDs) (7–9). These consist of a “pulse generator”, a small box containing a battery and an electronic control system which is implanted in the chest wall, and one or more leads which run through a large vein into the heart itself. The electrodes on these leads deliver electrical impulses to the heart muscle – in the case of a pacemaker, these ensure that the heart beats regularly and at an appropriate pace, while in the case of an ICD, a much stronger electrical shock is delivered as soon as the device detects a dangerously irregular heartbeat. Each lead typically has two or more electrodes made of platinum-iridium alloy, while platinum components are also used to connect the pulse generator to the lead (Figure 2).

Catheters and Stents

Catheters are flexible tubes which are introduced into the body to help diagnose or treat illnesses such as heart disease (10–13). The doctor can perform delicate procedures without requiring the patient to undergo invasive surgical treatment, improving recovery time and minimising the risk of complications. Many catheters incorporate platinum components: marker bands and guidewires, which help the surgeon guide the catheter to the treatment site, or electrodes, which are used to diagnose and treat some cardiac rhythm disorders (arrhythmias).

One of the most common coronary complaints in the developed world is atherosclerosis, the “furring up” of the artery walls with fatty deposits, which can lead to angina and heart attack (14). Blockages in the coronary arteries are often treated using a procedure called “percutaneous transluminal coronary angioplasty” (PTCA, also known as balloon angioplasty) (15, 16). This treatment uses a catheter with a tiny balloon attached to its end, which is guided to the treatment site then inflated, crushing the fatty deposits and clearing the artery. Afterwards, a small tubular device called a stent (Figure 3) is usually inserted in order to keep the newly-cleared artery open.

The advent of the implantable metal stent to prop open the artery after angioplasty reduced the occurrence of restenosis (re-narrowing of the artery) by more than 25 per cent. In 2003 the US FDA approved the first drug-eluting stent for use within the USA (17). This type of stent is aimed at further lowering the rate of restenosis following angioplasty procedures.

Platinum’s role in PTCA is to help ensure that the balloon is correctly located. First, the surgeon uses a guidewire to direct the balloon to the treatment site. This guidewire is made of base metal for most of its length, but has a coiled platinum-tungsten wire at its tip, which makes it easier to steer and ensures that it is visible under X-ray. Platinum is also used in marker bands, tiny metal rings which are placed either side of the balloon in order to keep track of its position in the body.

Stents are usually made of base metals (typically stainless steel or cobalt-chromium). However, in 2009, the American device manufacturer Boston Scientific introduced a cardiac stent made of a platinum chromium alloy (18–20). This stent has been approved in Europe, and the company is currently

<table>
<thead>
<tr>
<th>Medical device markets</th>
<th>Examples of application areas</th>
<th>Major medical device companies</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surgical instrumentation</td>
<td>Arthroscopic; ophthalmology; endo-laparoscopic; electro-surgical</td>
<td>Boston Scientific; Johnson &amp; Johnson; Stryker; Tyco</td>
</tr>
<tr>
<td>Electro-medical implants</td>
<td>Pacemakers; defibrillators; hearing assist devices; heart pumps</td>
<td>Boston Scientific; Biotronik; Medtronic; St. Jude Medical</td>
</tr>
<tr>
<td>Interventional</td>
<td>Stents; angioplasty; catheter ablation; distal protection</td>
<td>Boston Scientific; Abbott Vascular; Johnson &amp; Johnson; Medtronic</td>
</tr>
<tr>
<td>Orthopaedics</td>
<td>Spinal fixation; hip implants; knee implants</td>
<td>Biomet; Johnson &amp; Johnson; Stryker; Zimmer</td>
</tr>
</tbody>
</table>

Table I

Markets for Medical Devices and the Major Device Companies

Surgical instrumentation Arthroscopic; ophthalmology; endo-laparoscopic; electro-surgical.

Electro-medical implants Pacemakers; defibrillators; hearing assist devices; heart pumps.

Interventional Stents; angioplasty; catheter ablation; distal protection.

Orthopaedics Spinal fixation; hip implants; knee implants.

seeking approval from the US Food & Drugs Administration (FDA).

Catheters containing platinum components are also used to detect and treat some types of cardiac arrhythmia (21, 22). Devices called electrophysiology catheters (23), which contain platinum electrodes, are used to map the electrical pathways of the heart so that the appropriate treatment – such as a pacemaker – can be prescribed.

Other catheters with platinum electrodes are used for a minimally-invasive heart treatment known as radio-frequency (RF) ablation (24–26). Arrhythmias are often caused by abnormalities in the conduction of electricity within the heart, and it is often possible...
to cauterise part of the heart muscle in order to restore normal heart rhythm. For example, ablation is increasingly used to treat a very common heart problem called atrial fibrillation, in which the upper chamber of the heart (the atrium) quivers rapidly and erratically. Using a catheter equipped with platinum-iridium electrodes, the surgeon “ablates” or makes small burns to the heart tissue, causing scarring, which in turn blocks the superfluous electrical impulses which trigger the fibrillation.

**Neuromodulation Devices**

Neuromodulation devices deliver electrical impulses to nerves and even directly to the brain, treating disorders as varied as deafness, incontinence (27, 28), chronic pain (29) and Parkinson’s disease (30). Many of these devices are based on an extension of heart pacemaker technology, and they are sometimes referred to as “brain pacemakers” (31). Like heart pacemakers, they have platinum-iridium electrodes and may also incorporate platinum components in the pulse generator.

There are a number of different types of neurostimulation, depending on the condition that is being treated. Spinal cord stimulation (the commonest neuromodulation therapy) is used to treat severe chronic pain, often in patients who have already had spinal surgery. Small platinum electrodes are placed in the epidural space (the outer part of the spinal canal) and connected to an implanted pulse generator. The patient can turn the stimulation off and on, and adjust its intensity.

In deep brain stimulation (DBS) (32–34), the electrodes are placed in the brain itself. As well as pain, DBS may be used to treat movement disorders such as Parkinson’s disease, and it is being investigated as a potential treatment for a wide range of other illnesses, including epilepsy and depression. Epileptic patients can also be treated using a vagus nerve stimulation device (the vagus nerve is situated in the neck).

A cochlear implant (35–38) is used to restore hearing to people with moderate to profound hearing loss (many patients receive two implants, one in each ear). A typical device consists of a speech processor and coil, which are worn externally behind the ear, an implanted device just under the skin behind the ear, and a platinum electrode array which is positioned in the cochlea (the sense organ which converts sound into nerve impulses to the brain). The speech processor captures sound and converts it to digital information, which is transmitted via the coil to the implant. This in turn converts the digital signal into electrical impulses which are sent to the electrode array in the cochlea, where they stimulate the hearing nerve. These impulses are interpreted by the brain as sound. It is believed that around 200,000 people worldwide have received one or more cochlear implants.

At present, neuromodulation is expensive and is only available in a small number of specialist centres; even in developed countries only a small proportion of potentially eligible patients receive this treatment. However, neuromodulation can be used to help patients with common and sometimes difficult to treat conditions (such as chronic pain, epilepsy and migraine). Its use might therefore be expected to increase significantly in coming years as new indications for these therapies are established.

**Other Implants**

Platinum’s biocompatibility makes it ideal for temporary and permanent implantation in the body, a quality which is exploited in a variety of treatments in addition to the heart implants already discussed. Irradiated iridium wire sheathed in platinum can be implanted into the body to deliver doses of radiation for cancer therapy (39–41). This treatment takes advantage of platinum’s radiopacity to shield healthy tissues from the radiation, while the exposed iridium tip of the wire irradiates the tumour. Although this procedure is gradually being replaced by other forms of radio- and chemotherapy, it remains a useful weapon in the battle against cancer.

A more recent development is the use of coils made of platinum wire to treat aneurysms, balloonings in blood vessels caused by weaknesses in the vessel walls (42). If the blood pressure rises, the vessel may rupture, causing a haemorrhage. Although this can occur anywhere in the body, platinum is mainly used to treat aneurysms in the brain, where surgery is difficult and fraught with risk. Platinum is used because it is inert, easy to shape, and radiopaque.

This treatment was first introduced about 20 years ago. In the late 1980s, a doctor and inventor, Guido Guglielmi (43–45), developed a detachable platinum coil which could be used to treat brain aneurysms. Coils are delivered to the site of the aneurysm by microcatheter, then detached using an electrolytic detachment process; once in place, the coils help to coagulate the blood around the weak vessel wall,
forming a permanent seal (Figure 4). The coils, numbering between one and around thirty depending on the size of the aneurysm, are left inside the patient indefinitely. The Guglielmi Detachable Coil (GDC® Coil) device was approved in Europe in 1992 and in the USA in 1995, and by 2009 this and subsequent generations of platinum coil technology were being used in an estimated 30–40% of US patients treated for brain aneurysms.

**The Manufacture of Platinum Biomedical Components**

There are many technologies used to produce pgm components for biomedical applications, ranging from rod, wire, ribbon and tube drawing, to sheet and foil manufacture and highly precise Swiss-Type screw machining (micromachining) (see Figure 5).

Rod and wire are manufactured in diameters ranging from 0.125" (3.175 mm) down to 0.001" (0.0254 mm). Dimensional consistency is assured by laser measurement. Rod is used as the starting material for a variety of machine components, with most of the pgm parts being used in pacemaker, defibrillator and other electrical stimulation products. Wire products are used primarily in three applications:

(a) platinum-tungsten and platinum-nickel fine wires are used on balloon catheters as guidewires for positioning the catheter in exactly the right location;

(b) other pgm wires are used as microcoils for neurovascular devices such as treatments for brain aneurysms;

(c) platinum-iridium wires are also used as feed-through wires or connector wires used to connect the pacemaker lead to the pulse generator.

Ribbon is manufactured in the form of continuous strips of rolled wire in a variety of platinum alloys. Ribbon is often used in place of round wire to produce coils with minimum outside diameter, and is generally used for guidewire and microcoil applications. Ribbon is sometimes preferred over wire because wire can be harder to coil. It can also be used for markers instead of traditional cut tubing. Table II shows some typical specifications and applications for pgm rod, wire and ribbon.

Fine diameter platinum, platinum-iridium and platinum-tungsten tubing (0.125" (3.175 mm) internal diameter and below) cut to specific lengths is used for markers or electrodes on angioplasty, electrophysiology and neurological catheter devices, aneurism tip coils, feed-through wires used to connect the pacing lead to the pulse generator (also known as "the can") which houses the hybrid microelectronics and the battery, and pacemakers. Some applications of thin walled precious metal tubing are shown in Table III.

---

**Figure 4.** Detachable platinum coils being used to treat an aneurysm: (a) a microcatheter is used to deliver the platinum coils to the aneurysm; (b) the coils are detached using an electrolytic process; (c) more coils are added to fill the aneurysm and allow blood to coagulate, forming a permanent seal.

**Figure 5.** Micromachined parts made from precious metal alloys for biomedical device applications, with a pencil tip for scale.
Sheet and foil is mainly made from pure platinum, platinum-iridium alloys or rhodium. It can be shaped, formed and rolled to a variety of dimensions. Sheet or foil can be cut, formed and placed on a catheter for marking in a similar way to ribbon. Rhodium foil is used exclusively as a filter inside X-ray mammography equipment to enhance the viewing image.

**Table II**

**Specifications and Applications of Platinum and Platinum Alloy Rod, Wire and Ribbon Components**

<table>
<thead>
<tr>
<th>Applications</th>
<th>Types of component</th>
<th>Specifications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stimulation devices</td>
<td>Rod for manufacture of machine components</td>
<td>Diameters from 0.001&quot; (0.0254 mm) to 0.125&quot; (3.175 mm); Cut lengths from 0.02&quot; (0.508 mm)</td>
</tr>
<tr>
<td>Balloon catheters; stent delivery; stimulation leads</td>
<td>Guidewires; feed through wires; tip coils</td>
<td></td>
</tr>
</tbody>
</table>

**Table III**

**Specifications and Applications of Platinum, Palladium, Gold and Precious Metal Alloy Thin Walled Tube Components**

<table>
<thead>
<tr>
<th>Applications</th>
<th>Types of component</th>
<th>Specifications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Balloon catheters</td>
<td>Radiopaque marker bands</td>
<td>Inside diameter 0.0045&quot; (0.1143 mm) to 0.250&quot; (6.35 mm), (tolerance: ± 0.0005&quot; (0.0127 mm)); Wall thickness 0.001&quot; (0.0254 mm) to 0.005&quot; (0.127 mm), (tolerance: ± 0.0005&quot; (0.0127 mm)); Length 0.015&quot; (0.381 mm) to 0.200&quot; (5.08 mm), (tolerance: ± 0.003&quot; (0.0762 mm))</td>
</tr>
<tr>
<td>Electrophysiology catheters; stimulation devices</td>
<td>Electrode rings</td>
<td></td>
</tr>
</tbody>
</table>

Micromachined parts are very complex and very small – some are only 0.006" (0.152 mm) in diameter and barely visible with the naked eye (Figure 5). Fabrication must be extremely precise to maintain the necessary quality and dimensional tolerances, which can be as low as ± 0.0002" (0.005 mm). Highly specialised equipment and techniques must be used, such as computer numerical controlled (CNC) Swiss Screw machines and electrical discharge machining (EDM) (Figure 6). The automated high-production Swiss Screw machines are used to fabricate the main components and EDM is used to achieve the fine details required for many platinum parts.

Specialty metal micromachined parts (0.8" (20 mm) diameter and smaller) are made from a variety of materials including pure platinum, platinum-iridium alloys and gold plus non-precious metals and

**Table IV**

**Specifications and Applications of Platinum, Platinum Alloy and Rhodium Sheet and Foil Components**

<table>
<thead>
<tr>
<th>Applications</th>
<th>Types of component</th>
<th>Specifications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stimulation devices</td>
<td>Electrodes; machine components; tip coils</td>
<td>Thickness from 0.0007&quot; (0.018 mm); Width from 1.0&quot; (25.4 mm) to 3.75&quot; (95.3 mm)</td>
</tr>
<tr>
<td>X-Ray equipment</td>
<td>Imaging filters (rhodium foils)</td>
<td></td>
</tr>
</tbody>
</table>
alloys such as stainless steel, titanium, MP35N® cobalt-nickel-chromium-molybdenum alloy, Elgiloy® cobalt-chromium-nickel alloy, Kovar® iron-nickel-cobalt alloy, and materials such as Vespel®, Delrin® and Teflon® (see Table V for examples). These products serve device applications such as coronary stents, pacemaker and defibrillator pulse generator and lead components, heart valve splices, endoscopic catheters, blood gas analysers, kidney dialysis, and other medical device and related equipment.

Parts made from pgms are often complemented with a coating technology. Precious metal powders,

![Image](image.png)

Fig. 6. The production floor at Johnson Matthey’s Medical Products micromachining facility in San Diego, California, USA

### Table V

Applications and Materials for Precision Micromachined Components

<table>
<thead>
<tr>
<th>Applications</th>
<th>Precious metals*</th>
<th>Other materials, metals and alloys</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stimulation</td>
<td>Platinum; platinum alloys; palladium; palladium alloys</td>
<td>Nitinol; stainless steel; MP35N®, Haynes® alloy 25 (L605); polymers</td>
</tr>
<tr>
<td>Manufacturing fixtures</td>
<td>Platinum; platinum alloys</td>
<td>Stainless steel 303/304/316; polymers</td>
</tr>
<tr>
<td>Orthopaedic</td>
<td>Platinum; platinum alloys</td>
<td>Titanium; titanium alloys; stainless steel; ceramics</td>
</tr>
<tr>
<td>Cardiac implants</td>
<td>Platinum; platinum alloys; karat golds</td>
<td>Elgiloy®, Nitinol</td>
</tr>
<tr>
<td>Hypotubes</td>
<td>Platinum; platinum alloys</td>
<td>Stainless steel; Nitinol</td>
</tr>
<tr>
<td>Precision pins, tips and rollers</td>
<td>Platinum; platinum alloys; silver</td>
<td>–</td>
</tr>
<tr>
<td>Bushings, shafts, shims and spacers</td>
<td>Platinum; platinum alloys</td>
<td>Aluminium</td>
</tr>
<tr>
<td>Precision fixtures and assembly tools</td>
<td>Platinum; platinum alloys; Biomed™ series palladium-rhenium alloys</td>
<td>Brass; copper; Kovar®</td>
</tr>
</tbody>
</table>

*Platinum alloys used include platinum-iridium, platinum-10% nickel and platinum-8% tungsten
Titanium nitride or iridium oxide are applied to create a more porous surface structure. The creation of a porous coating reduces the electrical impedance from the lead to the battery and allows for a good electrical connection, while reducing the energy needed to run the battery. This helps the battery to last longer. Most pacing lead systems manufactured today have some form of porous surface. The end use applications for coated PGM parts are the same as described above for uncoated parts.

Anticancer Drugs

As well as its use in biomedical device components, perhaps platinum’s most remarkable and unexpected quality is its ability, in certain chemical forms, to inhibit the division of living cells (46). The discovery of this property led to the development of platinum-based drugs (47), which are now used to treat a wide range of cancers.

Although cancer remains one of the most feared diseases, its treatment has advanced rapidly since the late 1960s. Many types of cancer can now be treated very effectively using surgery, radiation and drug-based (chemo-) therapies. Chemotherapy drugs work by killing cells. They are designed to target cancer cells as specifically as possible, but inevitably cause damage to healthy cells as well, causing the side effects for which chemotherapy is well known.

One of the most remarkable advances in the last few decades has been the improvement in the survival rate of patients with testicular cancer – it is estimated that 98% of men with testicular cancer will be alive 10 years after their diagnosis. The platinum anticancer drug cisplatin (47) has played a vital role in making testicular cancer one of the most survivable cancers. This drug, along with its successor drug, carboplatin (48), is also widely used in the treatment of other common tumours, including ovarian, breast and lung cancer.

Summary

For over forty years, platinum and its alloys have been used in a wide range of medical treatments, including devices such as coronary and peripheral catheters, heart pacemakers and defibrillators. Newer technologies such as neuromodulation devices and stents also rely on the biocompatibility, durability, conductivity and radiopacity of platinum to make key components in a variety of forms. Platinum is used in pharmaceutical compounds that extend the lives of cancer patients. Medical device manufacturers and pharmaceutical companies continue to invest in new technologies to satisfy the need for advanced medical treatments in both the developed world and, increasingly, the developing world. Platinum, the other PGMs and their alloys will inevitably play a vital part in these developments.

Acknowledgements

The assistance of Richard Seymour and Neil Edwards, Technology Forecasting and Information, Johnson Matthey Technology Centre, Sonning Common, UK, in the preparation of this manuscript is gratefully acknowledged.

References

6 C. Walton, S. Gergely and A. P. Economides, Pacimg Clin. Electrophysiol., 1987, 10, (1), 87
9 D. S. Cannom, Am. J. Cardiol., 2000, 86, (9), Suppl. 1, K58
12 J. J. Rome and J. F. Keane, Prog. Pediatric Cardiol., 1992, 1, (2), 1
13 J. D. Moore and T. P. Doyle, Prog. Pediatric Cardiol., 2003, 17, (1), 61
15 A. S. Jacob, T. S. Goldbaum, A. D. Richard and J. Lindsay, Jr., Catheterization Cardiovascular Diagn., 1986, 12, (1), 64
17 US FDA, Recently-Approved Devices, CYPHERTM Sirolimus-eluting Coronary Stent – P020026, Approval date: 24th April, 2003; http://www.fda.gov/MedicalDevices/ProductsandMedicalProcedures/DeviceApprovalsandClearances/Recently-ApprovedDevices/ucm082499.htm (Accessed on 10th February 2011)


21 G. V. Irons, Jr., W. M. Ginn, Jr., and E. S. Orgain, Am. J. Cardiol., 1968, 21, (6), 694


29 P. L. Gildenberg, Pain Med., 2006, 7, Suppl. s1, S7


32 D. Tarsy, Epilepsy Behav., 2001, 2, (3), Suppl. 0, S45


34 P. Limousin and I. Martinez-Torres, Neurotherapeutics, 2008, 5, (2), 309


47 E. Wittshaw, Platinum Metals Rev., 1979, 23, (3), 90


Further Reading


“Materials and Coatings for Medical Devices: Cardiovascular”, ASM International, Materials Park, Ohio, USA, 2009


The Authors

Alison Cowley has worked in Johnson Matthey’s Market Research department since 1990 and currently holds the post of Principal Analyst. She is Johnson Matthey’s specialist on mining and supplies of the platinum group metals (pgms). She also conducts research into demand for pgms in a number of industrial markets, including the biomedical and aerospace sectors.

Brian Woodward has been involved in the electronic materials and platinum fabrication business for more than 25 years and is currently the General Manager of Johnson Matthey’s Medical Products business based in San Diego, CA, USA. He holds BS and MBA degrees in Business and Management and has been focused on value-added component supply to the global medical device industry.

© 2011 Johnson Matthey
The Manufacture of Continuous Glass Fibres

PRESENT TRENDS IN THE USE OF PLATINUM ALLOYS

by K. L. Loewenstein

Fibertech Consultants Limited, Fleet, Hampshire

One of the most exacting applications of platinum is in the production of glass fibre. This involves the rapid flow of molten glass at temperatures around 1300°C through a series of small orifices which must retain their size and alignment. Current trends in the design of platinum alloy bushings are towards a greater output of fibre per unit weight of platinum employed.

Almost all continuous glass fibres are manufactured by the attenuation of molten drops of glass exuding from nozzles located in the base of a special fibre drawing furnace called a bushing. Nearly all bushings are constructed from platinum alloy despite the high investment cost involved; one basic reason is that, when expressed in cost per kilogram of fibre produced, the use of platinum alloys is cheaper than the use of other metals, e.g., nimonic alloys. A second reason is that, at the operating temperatures required, metals other than platinum alloys do not have adequate mechanical strength. The main platinum alloys used are 10 and 20 per cent rhodium-platinum. The current trend of bushings design development aims at greater output of fibre per unit weight of platinum alloy employed.

Bushings are basically of two types:

(i) Remelt or marble bushings operating from cold glass marbles as the feedstock and fulfilling the dual functions of melting the glass and conditioning it to the correct temperature for fibre drawing (see Fig. 2).

(ii) Direct melt bushings, which are supplied with liquid glass near the operating temperature for fibre drawing and are attached to a feeder channel of a furnace into which the raw materials for glassmaking are fed (see Fig. 3).

Because of their dual function, remelt bushings are larger and weigh about twice that of direct melt bushings for the same output of fibre. For economic reasons, the majority of continuous glass fibres are now made from direct melt bushings and development of remelt bushings, except for the production of special fibre products, has ceased. This article concentrates on direct melt bushings, although much of their development can be applied to remelt bushings also.

Bushing Design

Bushing design is always in a state of development. With an average operating life of one year it is rare that an old bushing is replaced by one of identical design; the nozzle sizes may have been increased to achieve an increase in output, or some structural weakness may have been eliminated. But of all the changes over recent years the most important is related to the size, spacing, and the manufacturing technique of nozzles. This has led to much closer spacing of nozzles and also to a reduction in the use of platinum alloy per unit weight of fibre produced.

Originally, nozzles were made by taking the base plate, pressing small indentations in it where the nozzles were due to be located, and then building up solid nozzles by melting platinum alloy wire and placing it drop by
drop on the apex of each indentation. Periodically, during this build-up, each nozzle would be inserted in a small press-tool and the outside smoothed. When the nozzle build-up was completed the holes were drilled individually, including a counterbore if required. It can be readily appreciated that the manufacture of base plates for bushings by this technique was extremely laborious. Technically it placed a limit on the minimum distance between nozzles since access was required not only for the welder but also for simple tools needed for shaping the outside of the nozzle as well as for centering tools required for ensuring that the holes drilled in the nozzles were central to the nozzle itself.

The consistency of nozzle shape and location was improved by pre-manufacturing solid nozzles and inserting them into holes in a base plate followed by welding around each joint. But this method also called for access around each nozzle on both sides of the base plate and did nothing to enable more nozzles to be placed in a base plate of given area.

The objective of placing more nozzles in a given area of bushing base plates was brought about by the coming together of two separate developments. These were the demonstration that a nozzle counterbore was not necessary in order to achieve efficient production rates, and a new method of nozzle manufacture.

**Nozzle Manufacture**

As referred to above, most nozzles were originally made with a counterbore (see Fig. 4 (a)): This stemmed from the early period when bushings were made from pure platinum; due to the low glass/platinum surface tension the nozzles were frequently wetted by glass which travelled up the outside of the nozzle and across to adjacent nozzles, thus covering the underside of the base plate with glass. This seriously interfered with fibre drawing operations. By providing a counterbore, that is by thinning down the

---

*Photograph by courtesy of Owens-Corning Fiberglas*
wall of a nozzle at the exit, this problem was reduced. Although the subsequent introduction of rhodium-platinum alloys increased the glass/metal surface tension, the nozzle counterbores remained until the underlying reason for meniscus stability at the base of the nozzle was more clearly understood. It is now sufficient to say that, for rhodium-platinum alloys, provided the wall thickness at the base of a nozzle is 0.2 mm, then the glass will not normally wet the outside of the nozzle. Nozzle counterbores are therefore no longer needed. The fact that nozzles could now be drilled in one operation and that a counterbore was no longer necessary meant that the overall wall thickness of nozzles could be reduced.

The next development was a new method of nozzle manufacture based on coining and deep-drawing (see Fig. 5). The starting material was a base plate of such a thickness that it contained slightly more than all the metal required for the base plate of final thickness plus the metal needed for the drilled-out nozzles. By a process of coining, the metal in excess of that required for the final thickness of the base plate is concentrated in those positions where nozzles will be located; these are then deep-drawn in...
stages, with annealing between the stages when necessary to prevent fracture. This gives nozzles which have very accurate outside and inside dimensions as well as a very smooth bore; however, they are still closed at the outlet end. The outlets are opened by punching followed by smoothing the ends of the nozzles by surface grinding. A typical bushing of this type is shown in Fig. 6 before mounting in refractory brick and its metal frame.

**Rate of Flow of Glass**

This development clearly involves considerable work on special tooling and an understanding of the behaviour of platinum alloys when subjected to deep-drawing. The process itself could clearly be made simpler if the nozzles could be reduced in length. Having demonstrated that, for the stability of the fibre drawing process, the counterbore was no longer necessary and that metal could be saved by thinning down the nozzle walls, then the next stage was to aim to make shorter nozzles, which would, however, maintain a given rate of glass flow.

The rate of flow of a liquid through a pipe is given by Poiseuille’s equation:

\[ \frac{r^4 h}{12 \eta} \]

\( F \) is the rate of flow, \( r \) is the radius of nozzle bore in its narrowest cylindrical section, \( l \) is the length of the cylindrical section, \( h \) is the height of the liquid above the nozzle and \( \eta \) is the viscosity of the glass.

It is clear that if dimension \( l \) is reduced, then, in order to maintain the flow rate, dimension \( r \) must be reduced; if it is assumed that the clearance between adjacent nozzles is at a minimum for bushing manufacture then the distance between nozzles can also be reduced. Since several hundred nozzles are located in a bushing, even a small change in distance between adjacent nozzles can lead to a significant change in the number of nozzles that can be accommodated in a given base plate. For example, the base plate originally holding 400 of the longer nozzles, could readily be changed to accommodate about 600 of the shorter ones.

---

*Fig. 3 A typical direct-melt bushing. Above, side elevation, below, view from underneath with nozzle plate removed. Overall length of nozzle plate about 300 mm for a bushing with 400 nozzles.*
With improvements in the operating efficiency of fibre drawing processes it became clearly desirable to increase still further the number of nozzles in the base plate of a given bushing since this leads to savings in the use of platinum alloy as well as to other production cost savings. However, even after placing nozzles as closely as possible together on the base plate, this inevitably leads to an increase in the size of the base plate and the bushing overall. Since platinum alloys, at the operating temperatures of bushings are liable to creep, larger bushings lead to increasing danger of distortion of the bushing during operation.

Distortion of the bushing is most serious on the base plate, since this can affect the efficiency of fibre drawing. The most serious danger is what is colloquially referred to as "udderings". This is entirely due to creep at the operating temperature under the small load imposed by the load of glass above the base plate. There are several techniques for minimising this defect. The first is to use an alloy of low creep; for this reason 20 per cent rhodium-platinum is now preferred to the 10 per cent rhodium-platinum alloy. (The costs per unit volume of the two alloys are practically identical.) Alternatively, the use of zirconia-stabilised platinum will reduce creep. A second or additional method is to place internal stiffeners on the bushing base plate to prevent the sagging commonly experienced (one may be seen in Fig. 3). In some cases, indeed, the base plate has been provided with an inverted V in the longitudinal direction to provide stiffening. However, this method has a drawback since the base plate requires more platinum. As in most cases, a compromise has to be struck between bushing life and operating efficiency. But, even so, bushings

Fig. 4 Three examples of nozzle shapes giving the same production rates. It is clear that the nozzles in example (c) can be placed closer together, thus effecting a saving in platinum or allowing more nozzles per unit area of nozzle plate

Fig. 5 Schematic diagram of the manufacture of a bushing base plate by coining and deep-drawing
with over 1000 nozzles are now widely employed for many fibre products.

A further use of a platinum metal in association with fibre drawing is the use of nozzle shields. It was found some years ago that the stability of fibre drawing could be improved by placing radiation-absorbing shields between adjacent rows of nozzles. It was also found that the placing of these shields between alternate rows of nozzles was almost equally effective. Originally these fins were made of silver and attached to a water-cooled manifold acting as a heat sink. In some cases coolers made of flattened metal tubing were preferred, especially for use with bigger bushings, and have come into wide use. A suitable metal for these flattened tubes is rhodium-platinum alloy; a cheaper and equally effective metal is palladium.

Acknowledgement

The author wishes to thank Elsevier Scientific Publishing Company for permission to reproduce the diagrams from his book The Manufacturing Technology of Continuous Glass Fibres.
The Protection of Gas Turbine Blades

A PLATINUM ALUMINIDE DIFFUSION COATING

By R. G. Wing
Rolls-Royce Limited, Leavesden, England

and I. R. McGill
Group Research Centre, Johnson Matthey & Co Limited

Turbine blades in gas turbine engines operate at elevated temperatures and in highly oxidising atmospheres that can be contaminated with fuel residues and seawater salts. These components, which are expensive to produce, are subjected to high stresses during operation but must be totally reliable during their design life. An economic way to maintain blade properties is to coat the base metal superalloy with a protective layer capable of resisting both high temperature oxidation and hot corrosion. Conventional aluminide coatings are widely used for this purpose but platinum aluminides offer improved corrosion resistance. A collaborative exercise involving Rolls-Royce and Johnson Matthey has now resulted in the development of a platinum aluminide diffusion coating that offers some advantages over the commercial systems.

The gas turbine engine was first developed some forty years ago and by the early 1950s it was a commonplace power unit for both military and civil aircraft. However, in more recent years the gas turbine has become the prime power unit in many diverse applications including military and commercial land transport and marine propulsion systems. It is in the latter role where the greatest number of corrosion problems occur, these being particularly severe within the turbine section of engines used in ships, hovercraft and helicopters. In each of these engine applications a high ingestion rate of salt laden air is inevitable and, although sophisticated air filtration systems are employed in most cases, sea water residues can always be detected downstream of the filtration devices; in the most arduous conditions, such as those encountered during helicopter rescue missions, sea water itself can be ingested into the working engine, see Figure 1.

The combination of high turbine operating temperatures and the presence of ingested sulphate and chloride salts, apart from fuel contaminants such as sulphur and vanadium, can lead to severe blade attack which often results in the premature rejection of very costly turbine components; this attack is termed hot corrosion or sulphidation.

The majority of gas turbines in current service rely upon the use of conventional nickel aluminide diffusion coatings to protect superalloy turbine components from both oxidation and hot corrosion, but in the more extreme environments, predicted turbine blade lives are not being achieved. This breakdown of the protective coating can result in severe metal loss from the blade alloy, as illustrated in Figure 2.

There are three solutions to this problem:
1. Improve the filtration system and use high quality, low contaminant fuels
2. Develop more corrosion resistant blade alloys
3. Develop improved coating systems.

All of these areas have and are being examined but it is the latter solution that
Fig. 1 A rescue helicopter operating at sea level ingests a high level of salt water into the air intake with resulting contamination of compressor and turbine components by salt residues. During these operations several hours may be spent in such environments.

provides the most scope, and attention is specifically given to it in this article and particularly to the development of platinum aluminide coatings.

Although the development of more corrosion resistant blade alloys would appear to be an attractive alternative, the trend in recent years has been towards increased temperature capability but alloys designed for this purpose are inherently less corrosion resistant than their predecessors.

A General Background to Coating Technology

The conditions in which components operate in gas turbines are extreme, and the role of coatings is to protect turbine blades from the environment, ideally, for the design life of that part, whether it be creep or thermal fatigue that is seen as the limiting factor.

Currently, turbine entry temperatures range from approximately 650°C for industrial and marine engines to approximately 1300°C for the high performance aero engines, although in practice air cooling reduces the blade metal temperature, with 850 to 900°C being a realistic temperature range for the latter application. Additionally, in these days of rising costs, commercial operators require blades to last as long as possible with 5000 to 10,000 hours being typical for aero engines, and 100,000 hours for industrial turbines. It is against this background of blade metal temperatures and required life that coatings have been developed, but the effects of engine environment must also be considered.

The atmosphere in which turbine blades operate is generally highly oxidising with pressures of 10 to 20 atmospheres of oxygen, nitrogen, carbon dioxide and water vapour being seen in aero engines; additionally, fuel residues such as vanadium and sulphur, and ingested salts, can be present, with typical levels of 0.02 to 5 ppm of sea water salt being seen in
marine operation. Apart from the inherently corrosive nature of the turbine environment it can also be erosive when ingested dust is present or when carbon particles are released from the combustion chamber.

The prime role of a coating is to protect the blade substrate alloy against oxidation and hot corrosion (3, 4), but at the same time it must also possess some degree of erosion resistance and be able to tolerate minor impact damage. In addition it should withstand the mean blade stress due to the imposed centrifugal force (of the order of 150 MPa in some aero engines) and also resist the stresses caused by both thermal and mechanical fluctuations.

There are a variety of processing methods for producing turbine blade coatings but each must satisfy a number of essential requirements. The process must be able to produce uniform, controlled thickness coatings on complex geometry parts which are metallurgically bonded to the substrate alloy. Although gas turbine technology is inherently expensive, the cost of coating cannot be ignored and must be considered against the unit blade cost especially when coating small or solid blading.

The most widely used coating technique in current operation is that of pack cementation. This is generally considered a chemical vapour deposition process in which the element to be deposited is transferred to the surface of components by means of a volatile metal halide. The production of aluminate coatings by this method is one of the most economical and well proven process routes (5). An alternative technique for producing aluminate coatings is that of the slurry process, in which a slurry containing the required element is deposited onto the surface of the component; this is then dried and heat treated to achieve the required diffusion coating. However, this route has a number of disadvantages, a major area of concern being the handling of components during processing.

As well as the coatings that are formed by diffusion techniques, an important group of coatings, normally referred to as the MCrAlY overlays (M is cobalt or nickel), have been developed as corrosion resistant compositions and are applied to engine components by either physical vapour deposition (PVD) techniques or plasma spraying. Post coating processing is normally required to achieve metallurgical integrity of the coating.

Since current commercial coatings do not possess sufficient corrosion resistance, particularly when used in the more severe environments, coating technology is in a state of continual development. The areas of coating technology which are considered to offer the greatest potential for satisfying future engine demands are (i) constitutionally modified alumalides, (ii) platinum or platinum group metal alumalides (6, 7), (iii) constitutionally modified McrAlY overlays (8–11) and (iv) platinum or platinum group metal modified McrAlY overlays (12, 13).

At the present time interest is centred around further developments of McrAlY overlay and platinum alumalide systems. Examples of each of these systems are commercially available, and have shown in both engine and burner rig tests to offer a significant improvement in corrosion resistance over the conventional nickel aluminate diffusion coatings currently in widespread use. Apart from improved corrosion resistance, engine testing has also identified a major difference between the two systems in that aluminate coatings can exhibit an inherent lack of ductility when subjected to either thermal or mechanical cycling.

It should be emphasised that the generally accepted brittle coatings as understood by microstructure type, can withstand cyclic conditions in the engine as long as the lower blade operating temperature lies above the brittle to ductile transition temperature (DBTT) of the coating.

The low aluminium β-NiAl phase of an aluminate diffusion coating for example, can accommodate an approximate 1 per cent tensile strain at 650°C with true deviation from brittle behaviour occurring at 540°C (14); the equivalent temperature for transition from brittle to ductile behaviour for the high aluminium β-NiAl phase is approximately 815°C. The various temperatures quoted...
however, vary depending upon the actual constitution of nickel aluminide structures produced by different techniques. The DBTT for the MCRAIY overlays, however, generally lies between 350 and 500°C and hence these coatings can withstand a wider range of engine operating cyclic conditions.

Considerable evaluation of the MCRAIY and modified MCRAIY overlay coatings has taken place and a general understanding of the metallurgy of these systems is already known; the CoCrAIY overlays offer superior protection in hot corrosion environments while the NiCrAIY systems have the advantage in resisting high temperature oxidation. However, there is considerable impetus to develop these coatings further, and noble metal and other rare earth additions are being explored as alloying elements.

Although the overlay coatings are especially suited to military type engine applications where rapid and large temperature fluctuations can normally be expected, the modified aluminides and in particular the platinum aluminides are strong competitors in other engines where the reduced ductilities of these coatings can be tolerated. Platinum aluminides also show a real cost advantage when compared to the overlays for the same application. Further modification to improve the platinum aluminide system would appear to be a worthwhile objective.

Platinum Aluminide Coating Systems

The concept of the platinum aluminide coating system is historically attributed to Dr. Lehnert with the original British Patent being published in 1970 (15). The first commercial coating system, designated LDC-2, was developed jointly by Lehnert and Meinhardt (7) and marketed by a German company (Deutsche Edelstahlwerke Aktiengesellschaft); this first coating was produced by initially electrodeposition a platinum layer less than 10 microns thick onto a nickel base alloy and subsequently aluminiumising the platinised component for several hours at approximately 1050°C. Since 1970 the process has been licenced by the American based companies, Chromalloy American Corporation and Howmet Turbine Components Corporation, and each has
produced its own commercial platinum aluminide coating, designated RT-22 and LDC-2A respectively.

As far as the authors are aware the commercial platinum aluminide coating systems have been developed on an empirical basis, and involve the use of a platinum electroplating technique prior to a high temperature pack aluminising process, which is essentially the original specification for LDC-2. Although some modifications to the aluminising cycle and pack composition may have been implemented more recently, platinum is still deposited by conventional electroplating.

The commercially available platinum aluminide coatings have now been extensively evaluated in burner rig trials and selected test engines by Rolls-Royce, other engine manufacturers and independent research organisations, and have shown a substantial improvement in hot corrosion and oxidation resistance compared to conventional aluminide coatings. Although systems such as LDC-2A and RT-22 generally perform well in the turbine environment, certain aspects of the total processing route could be improved to achieve a more consistent product.

The deposition of platinum by electroplating is a simple and well established process but deposits are usually hard, may be highly stressed and are particularly prone to porosity. Additionally, poor cleaning procedures prior to electroplating can cause entrapment of non-metallic deposits between the substrate and the platinum overlay, leading to poor adhesion and incomplete diffusion of aluminium and platinum during the aluminising process. A typical example of this type of defect is shown in Figure 3.

Potentially the most serious of these problems is that prolonged times at high temperatures during aluminising, with subsequent slow cooling from the process temperature, can affect the morphology of the γ′(Ni₃Al) ageing precipitate of the substrate alloy. In some of the more complex superalloys these changes appear to be non-recoverable, and subsequent heat treatments do not restore the original γ′ morphology; testing has shown that some loss of creep strength can be associated with this effect.

An Improved Platinum Aluminide Coating Designated JMI-1

Both Rolls-Royce and Johnson Matthey recognised the possibility of improving the existing process to produce more consistent high quality platinum aluminide coatings, and embarked upon a collaborative exercise which involved Johnson Matthey in the research and development of a fused salt platinum deposition process compatible with nickel based superalloys and which offered potential as a production process. Similarly Rolls-Royce had the task of developing an aluminising process for platinum coated components that was compatible with retaining creep properties in blade alloys, and which produced a platinum aluminide coating that was equal or superior in corrosion resistance to those commercially available.

The technique of fused salt platinum plating was an obvious and attractive process to overcome the inherent problems of deposit adherence, porosity and hardness associated with an electroplating technique, and was consistent with the objective of developing a high quality platinum aluminide protective coating.
The process, refined and developed at the Johnson Matthey Group Research Centre for base metal cladding and electroforming (16), was developed further to achieve consistent high quality, even thickness platinum deposits on complex geometry superalloy substrates, an example of which is shown in Figure 4.

Additional effort was required during the early stages of development to establish an optimum substrate preparation and cleaning procedure which is now recognised as an essential part of the total fused salt deposition process. Having satisfied the initial requirements of the collaborative exercise, a critical examination of the post-platinising processes was undertaken by Rolls-Royce.

It was originally thought that a high temperature aluminising process would be needed to establish the characteristic platinum aluminate structure of the coating, but at the same time the process temperature should be kept below that at which irreversible changes occur to the ageing precipitate in the substrate alloy. Initial aluminising trials on platinum coated samples were carried out at 900°C but excessively thick platinum aluminate coatings were produced; similarly trials at 850°C and 800°C also produced thicker than required coatings. Subsequently, the use of a low temperature aluminising process successfully developed a platinum aluminate coating of the required thickness (50 microns).

The composition of the latter coating was considered inappropriate; this was later improved by a post-platinising high temperature vacuum diffusion treatment which was introduced prior to aluminising. This is a significant deviation from the accepted total processing route for commercial platinum aluminate systems, and rapid cool gas fan quenching from the diffusion temperature retains the existing γ'/morphology of the blade alloy.

Consequently Rolls-Royce was able to produce a platinum aluminide coating of consistent quality and microstructure, with no detriment to blade alloy properties. This development system was designated JML-1.

Fig. 4 A high quality platinum coating on the leading edge of a turbine blade illustrates the even coating that may be obtained by the fused salt plating technique × 20 approx.

Further development work around the high temperature platinising diffusion treatment produced a second system with different element profiles, this being designated JML-2.

The Structure of JML-1

Platinum aluminide coating systems that are developed on the surface of nickel based superalloys by diffusion processing can vary in their service performance, depending upon prior thermal and processing history. It has long been known that the degradation of any inherently protective coating is essentially a result of the natural response of the total substrate alloy/coating system attempting to establish thermodynamic stability. The degree to which this is achieved is obviously a function of service temperature and environment, and this has a direct influence upon the diffusivities of key elements within the total system.

The mechanism of degradation of conventional nickel aluminide coatings has been well established and involves the degeneration of protective NiAl to lower aluminides by (a) the diffusion of aluminium inwards to the substrate alloy and (b) the diffusion of aluminium to the coating surface to form and maintain the protective oxide, Al₂O₃. The initial concept of using platinum in such a coating system can be attributed to the belief that it would form the basis of a diffusion barrier system that would overcome the
Fig. 5 The elemental profiles for platinum, chromium, aluminium and nickel through a typical JML-1 platinum aluminate coating. Refractory elements originating from the substrate are normally restricted to the diffusion zone and the nickel aluminate structure.

problem of aluminium migration to the substrate, and hence maintain the high activity of aluminium at the surface where it is essentially required. It is now known that platinum itself does not act as a diffusion barrier for aluminium but more as a diffusion medium which, during processing, allows aluminium to establish a nickel aluminate subsurface structure and simultaneously generate a platinum-aluminium intermetallic skin. A knowledge of the constitution and structure of platinum-nickel-aluminate coatings developed by diffusion processing is an important aspect of this type of coating technology but has had little attention over the last ten years (6).

The collaborative effort between Rolls-Royce and Johnson Matthey, which resulted in the development of JML-1 and JML-2, combined respective technologies in an attempt to overcome some of the process and environmental performance limitations that may occur with commercially available platinum aluminides. The aluminising process used to generate the JML-1 structure is essentially a high activity, low temperature pack treatment evolved out of the necessity to retain the inherent high temperature properties of the substrate alloy, and to develop a coating structure which was consistent with good hot corrosion/oxidation resistance, while retaining reasonable ductility throughout its possible service temperature excursions. Following pack cementation the coating and substrate alloy undergoes the accepted solutioning and ageing treatments.
associated with alloy requirements. The final structure of JML–1 is therefore dependent upon the integrity and thickness of the initial platinum deposit, the cementation process parameters and the alloy heat treatment schedule. A typical elemental profile through a JML–1 coating structure is shown in Figure 5.

The constitution of JML–1 is by no means simple but may be treated for convenience as a series of intermetallics associated with the nickel-aluminium-platinum ternary system. Although a more ideal system would be the quaternary nickel-aluminium-platinum-chromium, chromium can be considered as a solid solution constituent associated with one or more of the nickel-aluminium, aluminium-platinum or nickel-aluminium-platinum intermetallics. The photomicrograph shown as Figure 6 is typical of the JML–1 structure.

Within the total coating thickness of nominally 60 microns, the first 2 microns of surface structure consists of a continuous layer of PtAl which is gradually replaced by 12 microns of a duplex [Pt(Ni)]12Al10 + PtAl structured zone. The composition of the next 6 microns would indicate a duplex PtAl + [Ni(Pt)Al] zone. This top layer, with a combined thickness of 20 microns, generally shows no etching characteristics and can be easily identified.

The central portion of the JML–1 coating structure consists of the β-NiAl intermetallic occupying approximately 25 microns of the total coating thickness. The first 15 microns of this layer incorporates platinum as a solid solution component substituting for nickel in both the Al-rich hyperstoichiometric β-NiAl and the Ni-rich hypostoichiometric β-NiAl. The remaining 10 microns of this 25 micron central layer is virtually free of platinum and is essentially Ni-rich β-NiAl. The finger-like sub-structure (the diffusion zone) below β-NiAl occupying some 15 microns of the total coating is sequentially composed of β-NiAl + αCr and y'(Ni3Al) + αCr, together with intermetallics and carbides rich in the refractory elements. The coating finally terminates with the alloy microstructure of γ'(solid solution matrix) + γ.

A number of important observations can be made regarding the diffusion of elements such as tungsten, molybdenum, titanium, cobalt, nickel and chromium within the total coating structure after complete processing. Titanium has greater diffusivity through platinum-nickel intermetallics than the refractory elements tungsten and molybdenum. A similar behaviour is also apparent for cobalt. Although nickel can effectively diffuse throughout the β-NiAl structures, the intermetallic PtAl2 behaves as an effective diffusion barrier restricting the movement of nickel to the surface, thereby allowing unrestricted growth of protective Al2O3. The results of long-term high temperature stability tests on JML–1 would suggest that the latter situation is maintained, indicating that the stoichiometric intermetallics of platinum and aluminium are effective diffusion barrier materials when operating under hot corrosive gas conditions. The ability of titanium to establish a relatively high composition profile throughout the coating structure is undoubtedly beneficial to coating performance. Refractory elements such

Fig. 6 A JML–1 coating structure developed on a MAR-M002 superalloy substrate consists essentially of an outer unetched layer of platinum-aluminium intermetallics underlain by a zone of β-NiAl × 350 approx.

as tungsten and molybdenum, although essential solid solution strengtheners, have an adverse effect upon resistance to hot corrosion and it is thought that the ability of the JML-1 system to restrict these refractory element mobilities gives rise to the improved performance over conventional aluminate systems.

The relatively high level of chromium throughout the platinum aluminate structure is considered an additional important benefit for the system, and is different to that of some commercial platinum aluminate coatings.

Within the platinum-aluminum binary system there are a number of intermetallic compounds. Due to the kinetics of the aluminising process, only the intermetallics PtAl3, Pt3Al, and PtAl are generally found in aluminised structures. Only the molecular volume of PtAl3 shows any resemblance to the 'ideal' volume predicted by linear correlation between volume and composition. Aluminum-rich intermetallics form with considerable expansion; the platinum-rich with a contraction. Coating systems based upon the platinum-aluminum binary and which specifically generate PtAl3 at the surface constituting a significant portion of the platinum aluminate layer, may undergo as much as 10 per cent surface volume contraction during service as a result of degeneration from PtAl3 to PtAl. It is unlikely that such a volume change within an inherently brittle matrix could be accommodated without void formation or cracking. The JML-1 processing schedule develops a coating with a Pt3Al surface layer which, although undergoing a 9 per cent volume contraction during degeneration to PtAl, has shown little evidence for surface cracking.

Platinum aluminate systems in general may well have the potential for application in both hot corrosion and oxidation environments making them suitable as protective coatings for high strength alloys in industrial, marine and aero gas turbines. Similarly their resistance to sulphidation at high temperatures may well be a property that can be exploited in other industrial process environments normally considered corrosive to the best cast or wrought nickel based alloys. The key to the performance of platinum aluminites is, however, very much dependent upon achieving the optimum coating composition and structure through controlled processing. The development coating JML-1 is undoubtedly an advance in coating technology.

**Burner Rig Tests**

The gas turbine simulator, more frequently referred to as a 'burner rig', is generally used for hot corrosion studies and consequently sets out to simulate temperatures and atmosphere rather than specific dynamic parameters. Unfortunately, as a complete understanding of the important parameters in hot corrosion is limited at the moment, there is a wide variation in operation conditions to be found in various burner rigs operating throughout the world and indeed in the individual design from rig to rig; it is also difficult, at the present time, to accurately cross-correlate results from different rigs. The burner rig is, therefore, essentially a comparative corrosion test for evaluation of gas turbine alloys and coatings, but is a vital link between laboratory evaluation procedures and full engine testing.

The JML-1 platinum aluminate coating system has undergone exhaustive assessment in Rolls-Royce and in other independent burner rig trials, one of which was carried out at the Johnson Matthey Group Research Centre. The results from these trials have shown the JML-1 system to considerably outperform the conventional aluminate coatings.

The results of a burner rig trial carried out by Johnson Matthey are shown for example in Figure 7, and a schematic drawing of the burner rig is detailed in Figure 8.

The level of salt as residue passing through the combustion section was approximately 2.4 ppm by weight and the level of sulphur dioxide injected was 1.56 litres per hour. The rig is fuelled for convenience by a mixture of natural gas and air with an air : fuel ratio at the carousel section of approximately 30 : 1. Thermal cycling, from test to room temperature, was carried out once every hour.

Two commercial alloys, namely IN738 and
MAR–Mo02, were chosen as suitable and representative gas turbine alloy substrates to examine the performance of the JML–1 coating. Under burner rig conditions, all coated systems JML–1/N-738 and JML–1/MAR–Mo02 show obvious outstanding performance. The JML–2 system, a modification of the JML–1 system, designed to achieve a more even platinum distribution throughout the coating structure, clearly provides protection at higher temperature engine operation but has limitations as a system for lower temperature hot corrosion resistance.

It is also important to recognize the variation in coating performance as a function of alloy substrate. The coating and substrate are a single system, but the individual properties of each must be considered when matching the two. All elements in the substrate can, and usually do, diffuse into the coating and can influence oxidation and hot corrosion rates. Evaluation of similar coating systems must,
therefore, consider the effect of different substrates and care must be exercised in comparing results where different substrate alloys have been used.

**Engine Tests**

Apart from burner rig tests, platinum aluminide coatings have been widely evaluated in a variety of Rolls-Royce engines, and in all instances they have shown a significant improvement in corrosion resistance over conventional aluminides; a similar improvement is also shown by the MCrAlY overlay systems in this respect. Figure 9 shows the type of results obtained from a 500 hour engine test.

The JML-1 and JML-2 coatings have been evaluated principally in engines for marine applications; JML-1 in particular has been seen to perform as well as the commercial LDC-2 and RT-22 systems, and in some specific engines it has shown improved corrosion resistance. One reason that may explain the improved performance of the JML-1 system is that its compositional difference from the commercial platinum aluminides results in the production of an inherently more corrosion resistant coating. However, it is possible that other factors such as erosion resistance or ductility play a significant role in resisting coating degradation.

**Future Developments**

At the present time a number of industrial and marine engines in the United States of America are operating with blades coated with platinum aluminide systems as a standard production specification. A number of other countries including the United Kingdom are expected to follow suit as more and more engines are required to operate in aggressive marine environments with lower grade fuels. It is therefore important to further evaluate the most promising platinum aluminide coatings for the applications intended, and to examine ways of improving these systems.

Platinum aluminides are inherently less ductile than the MCrAlY overlays and cannot compete across the board with these systems, but further modification of the noble metal systems to overcome this problem could be a worthwhile task, and the potential rewards may be substantial.

Future developments in gas turbine technology will require even higher temperature capabilities from turbine blade materials in the search for higher performance.
and improved specific fuel consumption (SFC) (17). These goals will require new blade alloys such as single crystal, oxide dispersion strengthened and directional eutectic materials, and the introduction of these into engine operation will pose certain problems as to whether currently available coatings will provide adequate protection; there is still tremendous scope for further coating development.

Acknowledgements

The authors wish to thank their colleagues who have directly or indirectly contributed to this paper. The alloy designation MAR-M2002 is a trademark of the Martin Marietta Corporation and the alloy designation IN 738 is a trademark of Inco Ltd.

References


The Platinum Group Metals in Society

A general concern about future supplies of industrially important materials was demonstrated in the interest shown in a recent London conference, entitled "Strategic Metals in the 1980s". The internationally recognised authorities who spoke included Mr. D. R. Dumenil, an Executive Director of Johnson Matthey & Co Limited, who presented a paper on the platinum group metals.

Despite the relatively small quantities of platinum group metals that are available, the remarkable properties of these metals bring great benefits to industry, and to society in general. Due mainly to increased industrial use, but also to a growing interest in all things that are both rare and precious, the demand by the Western World—including Japan—has increased four-fold over the past twenty years, with purchases of newly mined platinum, palladium and rhodium now being made at an annual rate of about 170 tonnes.

In addition to presenting an account of some of the many strategically important industrial processes that rely on the platinum group metals, most of which will be known to regular readers of this journal, reference was also made to the use of the metals as jewellery materials. Increasingly, jewellers and their customers are becoming aware that the colour of high-purity platinum enhances precious stones, while its strength enables the most delicate mounts to hold stones securely. Although platinum is the most important for this purpose, palladium is used as an alloying element, particularly in Japan, and electroplated rhodium is used to provide a brilliant protective surface on other metals.

In the foreseeable future, it is improbable that there can be any dramatic change in the world's dependence on South Africa and the Soviet Union for supplies of the platinum group metals, but in South Africa alone the reserves amount to over 300 years production. At present 10 tonnes of the Rustenburg ore yields little more than one and a half ounces troy of platinum metals, so a vast producer industry is already committed to satisfying the needs of the platinum users. Thus, providing there is a reasonable guarantee that consumption will continue at an adequate level, the underground reserves can be made available on the surface for a continuing expansion of use.
The Ammonia Oxidation Process for Nitric Acid Manufacture

EARLY DEVELOPMENTS WITH PLATINUM CATALYSTS

By L. B. Hunt, M.Sc., Ph.D.

It is little more than fifty years since the first manufacture of nitric acid by the oxidation of ammonia over a platinum catalyst. Ostwald's original industrial plant had an output of some 100 tons of acid a year; today the world capacity for nitric acid manufacture by this process is about ten million tons a year. This article traces the beginnings and early developments of the process until it became commercially established.

During the latter years of the nineteenth century discussion began to arise among men of science who were interested in the broader issues of their subject on what later became known as "The Nitrogen Problem". Typical of the expositions which now and then reached even the public press was the Presidential Address given by Sir William Crookes to the British Association for the Advancement of Science at its Bristol meeting in September 1898. Crookes was concerned to show that at the prevailing rate of increase of population the world's supplies of what would soon prove insufficient, and that the land would not continue to produce the same yield year after year unless adequate quantities of nitrogenous manure were ploughed back. He appealed to the chemist to help remove the fear of famine by establishing a means of fixing atmospheric nitrogen, since the only available source—Chile saltpetre—might be exhausted in a comparatively short period of years.

The Fixation of Nitrogen

This problem, of obtaining from the unlimited supplies of uncombined nitrogen in the atmosphere those compounds—principally ammonia and nitric acid—required for agricultural needs, was soon intensified by the realisation in a number of European countries that a precisely similar need for assured supplies of nitric acid existed in the manufacture of explosives, and that in the event of war the Chile nitrites might well prove to be inaccessible to one side or the other.
Frederic Kuhlmann

Many years before Ostwald's time, Kuhlmann had demonstrated the possibility of obtaining nitric acid by the oxidation of ammonia over a platinum catalyst.

This is not to say that such thoughts inspired governmental action in any part of Europe; they were, in fact, confined to but a handful of scientists who could foresee their countries' long-term needs. One such man was Professor Pfeffer, the famous botanist, who in 1901 expressed his concern about the need for supplies of fixed nitrogen to his colleague in the University of Leipzig, Professor Wilhelm Ostwald. At this time Ostwald had occupied the Chair of Chemistry at Leipzig for some fourteen years and had built up a school of physical chemistry, devoting much of his energy to investigating the effects of catalysts on chemical reactions. His response to Pfeffer's representations was immediate; it was obviously his duty as a chemist to play his part in making his country independent of Chile saltpetre, and in obtaining nitric acid from other sources.

Two possible lines of investigation presented themselves. Either free nitrogen and oxygen from the air could be combined, or ammonia, then readily available from the gas industry, could be oxidised to give nitric acid. As it seemed more simple to re-combine nitrogen which was already fixed than to fix free nitrogen, Ostwald decided to give his attention to the oxidation of ammonia.

This reaction was not unknown, and in fact had been proved possible on a laboratory scale. As long ago as 1789 the Rev. Isaac Milner, F.R.S., President of Queen's College and first Jacksonian Professor of Natural Philosophy in the University of Cambridge, had presented a paper to the Royal Society entitled "On the Production of Nitrous Acid and Nitrous Air". In this Milner described a series of experiments in which he had passed "volatile alkali" (ammonia) over "caix of manganese" contained in a gun-barrel heated to redness. The product was found to be "highly nitrous", and the presence of "nitrous air" was confirmed by the appearance of red fumes on mixing with the atmosphere or with "dephlogisticated air". Milner continued:

"I have since frequently repeated this experiment, and have always (as I must now say) succeeded. Much depends on the kind of manganese employed, much on the heat of the furnace, and much on the patience of the operator; as these are varied, there will be great variations of the product. . . . In general, I made use of clean gun-barrels with which no previous experiments had been made. The manganese was used in rough powder; for when it is too finely powdered, the tube is choked and the air cannot pass."

Kuhlmann and his Patent

More fundamental and extensive work had been carried out by Frederic Kuhlmann, the founder of the great chemical enterprise Etablissements Kuhlmann. Born at Colmar in 1803, Kuhlmann had been a student of Vaquelin and had been nominated by him to the newly-formed Chair of Industrial Chemistry at the University of Lille at the early age of 21.

He knew from the work of Lavoisier that ammonia was composed of nitrogen and hydrogen, and that nitric acid was composed of these two elements together with oxygen. He was also familiar with the early discoveries in catalysis made by Humphry and Edmund...
A Prophecy and its Fulfilment

"If in fact the transformation of ammonia to nitric acid in the presence of platinum and air is not economical, the time may come when this process will constitute a profitable industry."

So wrote Frédéric Kuhlmann in 1838. Today the great chemical firm that he founded, Etablissements Kuhlmann, is among the leading producers of nitric acid by the oxidation of ammonia in their plant at La Madeleine-lès-Lille.

Davy and by Döbereiner, as well as with the work of Dulong and Thenard, reported in 1829, on the catalytic activity of the platinum metals in bringing about the combination of oxygen and hydrogen. He was also greatly interested in the part played by nitrogen products in agriculture (and in fact in later years carried out investigations on the use of ammonium salts as fertilisers on his own estate).

With this as his background, Kuhlmann went to work vigorously on the nitric acid problem, and found that by passing a mixture of ammonia and air over platinum sponge heated to about 300°C in a glass tube he obtained nitric acid. He filed a patent application for this invention in 1838.

At this time saltpetre was readily and cheaply available, and the new process could not offer any commercial advantage, but in the course of a paper given to the Société des Sciences de Lille in the same year, Kuhlmann made these prophetik remarks:

"If in fact the transformation of ammonia to nitric acid in the presence of platinum and air is not economical, the time may come when this process will constitute a profitable industry, and it may be said with assurance that the facts presented here should serve to allay completely any fears felt by the government on the difficulty of obtaining saltpetre in sufficient quantities in the event of war."

Ostwald's Experimental Work

To return to Ostwald, it was clear to him that the theoretical basis of the ammonia oxidation reaction would have to be elucidated before it could be developed on a large scale, and experiments were begun by Dr. Eberhard Brauer, at that time Ostwald's private assistant. The first experiments were made using a clean glass tube only a few millimetres in diameter containing platinised asbestos. Ammonia and air were passed over the catalyst in known quantities and with known velocities, and it was at once clear that the conversion to nitric acid was practicable and relatively simple to carry out, although some difficulties lay in the absorption of the reaction products. The historic apparatus used at this stage is shown overpage.

The first experiments using platinised asbestos gave only small yields and a platinum-lined tube proved little better. A new reaction tube was therefore made, consisting of a glass tube 2 mm in diameter in which was coiled a strip of platinum about 20 cm long. The whole tube was heated to redness, and the first experiment gave a conversion of more
Ostwald and Brauer, and here a pilot plant was developed. By 1904 the three converters illustrated below had been built and operated, and it was decided to erect a larger-scale plant at the Gewerkschaft des Stein köhlenbirgwerks Lotthringen at Gerthe, near Bochum, to produce 300 kg per day of nitric acid.

This plant was brought into operation in May 1906 and fully proved the feasibility of the process. A larger-scale plant was then designed and built, and by the end of 1908 was producing some three tons of 53 per cent nitric acid per day.

The catalyst used at this time consisted of a roll of corrugated platinum strip about 2 cm wide and weighing about 50 g, heated initially by a hydrogen flame. The life of the

The apparatus in which Ostwald and Brauer first investigated the ammonia oxidation process.

than 50 per cent. Attempts to increase the yield by reducing the gas velocity or increasing the time of contact gave just the opposite result, while increasing the gas velocity gave a conversion of 85 per cent. Ostwald, after several days brooding on this apparent anomaly, hit on the explanation; the nitrogen oxides formed could decompose to free nitrogen and oxygen if the time of contact between the gases and the catalyst were lengthened. Corroboration of this conclusion lay in the fact that unburnt ammonia was never detected behind the contact zone.

This determined the course of further experiments, which included investigations on the effects of variations in the ammonia: air ratio, in the time of contact and in the temperature of the catalyst. Thus were laid the foundations of a technical process for producing nitric acid from ammonia, but the translation from idea to practice presented many problems before the project was brought to fruition.

A small factory was made available to
catalyst was no more than a month or six weeks. The disadvantages of the process included the relatively large amount of platinum required per unit of acid produced, and the uncertainty of temperature control of the catalyst, but improvements were not long wanting.

The Platinum Gauze Catalyst

Dr. Karl Kaiser, of the Technische Hochschule, Charlottenburg, attacked the problem, and filed patents in 1909 covering the pre-heating of the air to 300 or 400°C and the use of a layer, usually four in number, of platinum gauzes. He was the first to employ platinum in the form of gauze, and it is a tribute to his experimental skill that the precise form of gauze he settled on—wire 0.06 millimetre diameter woven to 1050 mesh per square centimetre—is still very largely employed. By 1912 Kaiser had a pilot plant in operation at Spandau, Berlin, but while this was inspected repeatedly by British, French and American industrialists, he failed to interest them in his process, although a plant was erected at Kharkov in Russia.

A little earlier, in 1907, Dr. Nikodem Caro, of the Bayerische Stickstoffwerke A.G., and Adolph Frank, the joint inventors of the cyanamide process, had claimed a method of producing nitric acid from ammonia by means of a catalyst consisting essentially of thorium oxide admixed with small amounts of rare earths such as cerium oxide. This process failed, chiefly because the catalyst sintered and rapidly became impermeable, but further work was carried out by Caro and Frank’s son Albert, who was then a chemical engineer at the Bayerische Stickstoffwerke. Several patents were filed during 1914, the process being based upon a single platinum gauze which was electrically heated. Progress was slow for a time, and numerous experimental plants failed, but the outbreak of war gave a much greater urge to the project and by 1916 the picture had changed radically. The Frank and Caro converter had by then been engineered by the Berlin-Anhaltische Maschinenbau A.G. (BAMAG), who had constructed more than thirty plants, first for the supply of nitric oxide to lead chamber sulphuric acid plants and later for nitric acid production. The single platinum gauze was subsequently replaced by multiple gauzes, and the electrical heating was discontinued. This type of plant supplied all the nitric acid required for explosives in Germany during the later years of the war. The converter had a diameter of 20 inches, the catalyst consisting of a layer of three platinum gauzes woven from 0.006 inch diameter wire of 80 mesh to the linear inch, operating at about 700°C. The three gauzes were spot welded to a platinum grid and retained in place by embedding in asbestos. A much greater catalyst life was obtained in this design of plant, extending to six months provided that conditions were uniform and that the gases were free from impurities that might have a poisoning effect.

Initial Production in America

At the beginning of the war the United States possessed no source of nitric acid other than Chile saltpetre, and it became distressingly evident that the nation was dependent upon a foreign country in this respect, while the production of nitric acid from this starting-point required large quantities of sulphuric acid, already in short supply.

Cyanamide had been manufactured at Niagara Falls since 1909, and in 1916 the first American plant for the oxidation of ammonia produced from cyanamide was established by the American Cyanamid Company at Warners, New Jersey. The catalyst employed was a single platinum gauze, electrically heated. In the meantime, the Ordnance Department had decided to take action, and Dr. C. L. Parsons, of the Bureau of Mines, was asked to investigate European methods for nitrogen fixation. As a result the American Cyanamid Company was requested, in 1917, to form a subsidiary company, Air Nitrites Corporation, to act as agent for the United States Government for the construction and operation of a plant at
Muscle Shoals, Alabama, to produce 110,000 tons a year of ammonium nitrate. This plant comprised some seven hundred catalyst units, each containing a single rectangular platinum gauze woven from 0.003 inch diameter wire, 80 mesh, and heated electrically to 750°C. The total weight of platinum was a little over 300 oz, and the loading ratio about 1 kg per daily ton of ammonia.

A smaller plant was also erected by the government at Sheffield, Alabama, and here a different approach was adopted to the catalyst design, aimed at conserving a greater proportion of the heat of reaction. Four layers of 80 mesh platinum gauze were rolled into a cylinder, which was heated by torch for a short time; on passing the ammonia-air mixture the reaction started at once and then became self-sustaining for many months.

This construction was later abandoned, however, on account of the difficulties in installing and operating the gauze cylinder.

**Developments in Great Britain**

There had been little or no commercial interest in nitrogen fixation in Great Britain before the outbreak of war in 1914, and throughout the war period the supply of nitrogen products for munitions depended almost entirely on Chilean nitrate. Towards the end of the war, ammonium nitrate for the manufacture of Amatol was being prepared at the rate of a million tons per year by the double decomposition of sodium nitrate and ammonium sulphate, a process based on F. A. Freeth's studies of the phase rule.

There were, however, a number of attempts to make nitric acid by the direct oxidation of ammonia, either from gas-liquor or cyanamide. An Ostwald plant was set up at Dagenham Dock by the Nitrogen Products Company in 1916-1917, but never achieved successful operation. The Gas Light and Coke Company developed a plant at Beckton using a pad of three or four flat platinum gauzes as catalyst, and attained an output of a ton of nitric acid per day.

A systematic investigation was undertaken, at the instigation of the Nitrogen Products Committee, by Professor J. R. Partington and Dr. L. H. Parker, and was carried out in the laboratory of the Munitions Inventions Department. An effective design of converter was evolved, employing either an electrically heated pad with two gauzes or a thicker pad that was self-sustaining in temperature when reaction had been established. Somewhat similar converters were constructed by Brunner Mond & Company and by the United Alkali Company, the latter of a pattern that is still in widespread use in the sulphuric acid chamber plants, constructed of enamelled cast iron with an integral tubular heat exchanger.

Although it came too late to be of service in the war, the decision taken in 1917 to erect a synthetic ammonia plant using the Haber-Bosch process led directly to the building of the Billingham plant by Synthetic Ammonia and Nitrites Ltd. (now Imperial Chemical Industries Ltd.). The ammonia plant first came into operation in December 1923 and the nitric plant—the first successful large-scale plant in this country—during 1927.

Although the process remains unchanged in principle—and even in some details such as the mesh sizes of the gauze pads—the size and complexity of the plant units has been tremendously increased. The first commercial operation at Lothringen Colliery produced 300 kg per day of weak acid. The most recently erected single units, working at a pressure of 120 lb. per sq. in. have an output of 250 tons per day, measured as 100 per cent acid. From the 50 g of corrugated foil in an Ostwald unit, the weight of platinum in a single converter has steadily increased until it may now be 15 kg or more, but the ratio of platinum used per daily ton of ammonia burned has fallen from over a kilogram to 250 g or less.

The next issue of 'Platinum Metals Review' will include an article by Mr. A. W. Holmes, of Imperial Chemical Industries Limited, Billingham, describing the technical and economic factors that have influenced the development of the ammonia oxidation process in more recent years.
ferrocinium, and c) decasubstituted neutral metalloccenes, \((C, R_1)_n M\), where \(R=\text{phenyl or}
\text{benzyl and } M=\text{Sn(II) or Ge(II)}\). Examples of
each type were active in markedly inhibiting
tumour growth and induced severe cytological
and histological changes in the tumours treated,
which suggested that the complexes interfere
with nucleic acid metabolism. Reaction of the
titanium complex resulted in \([\text{Cp}_2 \text{Ti}]^+\)
coordinated to purine nucleosides through both
monodentate N7 and N7-O6 chelation. The
vanadocene moiety appears to bind in a labile
outer-sphere fashion to phosphate groups.
Doses of \([\text{Cp}_2 \text{TiCl}_2]\), are limited by liver toxicity.

Ruthenium and platinum compounds may be
used to direct radiosensitising molecules to
DNA, according to Professor Nicholas Farrell
of the University of Vermont. This approach is
particularly useful in radiotherapy applied to
hypoxic or anoxic areas of tumours, where
radiation is less effective. Studies on the radia-
tion killing of cells indicate that metal com-
plexes ligated with nitroimidazoles are more
active than either the metal or ligand precursor
molecules alone and so point a way to the
design of new agents.

The ruthenium isotope, \(^{197}\text{Ru}\), has excellent
radiophysical properties for use in diagnostic
imaging agents. Its \(\gamma\)-ray is easily collimated by
existing radioscintigrapic cameras and its
3-day half-life provides adequate time for syn-
thesis and quality control. Dr. Suresh
Srivastava of Brookhaven National Laboratory
presented the first clinical studies of a liver-
imaging agent using a complex with disopropyl
carbamoylmethyl iminodiacetate, which proved
very effective in imaging the livers of neonates
suspected of liver dysfunction. Radiolabelling
studies also showed that some Ru(III) com-
plexes can be bound to transferrin and carried
to receptor sites on tumours. The metal ion is
fixed inside the cell, possibly by a redox
mechanism, while the transferrin is released.

The symposium discussions concerning the
various approaches to ruthenium-containing
anti-cancer drugs reflected the versatility of this
element in synthesis, electron transfer, and
even photochemistry. These properties, cou-
pled with the affinity of ruthenium’s intermediate
oxidation states for imine nitrogens, facilitate
DNA targeting for both chemotherapeutic and
radiosensitising agents. Finally, the existence of
isotopes with desirable properties for diagnostic
imaging indicates that exploration of the
medical applications of ruthenium is likely to
produce useful pharmaceuticals.

Lean-Burn Oxygen Sensor Material
PLATINUM CATALYST IMPROVES RESPONSE TIME

Oxygen sensors are widely used as auto-
mobile engine control devices in order to obtain
an optimised balance of exhaust emissions, fuel
economy and vehicle drivability, and generally
this is achieved by controlling the air to fuel
ratio at the stoichiometric mix of \(14.7:1\). Now
there is increasing interest in controlling the air
to fuel ratio away from the stoichiometric point,
in the lean-burn region, with the aim of increas-
ing engine efficiency and decreasing nitrogen
oxides emissions.

Lean-burn oxygen sensors are generally
classified as either semiconducting or
electrochemical pumping. The former are small,
simple, low cost devices which are based upon
the resistivity changes that take place in oxide
semiconductors as the partial pressure of
oxygen in the surrounding atmosphere varies.

A recent paper by C. Yu, Y. Shimizu and H.
Arai of Kyushu University, Fukuoka, Japan,
reports on their investigation of several species
of magnesium-doped \(\text{SrTiO}_3\) in the exhaust
gas resulting from air-propane combustion con-
taining water vapour ("Mg-Doped \(\text{SrTiO}_3\) as a
Lean-Burn Oxygen Sensor", \textit{Sens. Actuators},
1988, \textit{14}, (4), 309–318). At temperatures be-
 tween \(600\) and \(800^\circ\text{C}\), the highest sensitivity to
oxygen in the lean-burn region and the lowest
sensitivity in the rich-burn region was shown
by \(\text{SrTiO}_3-\text{Mg}_{10} \times \text{O}_{12-\delta}\), and therefore it was con-
sidered to be a suitable material for a lean-burn
oxygen sensor. However the response time was
about 1.5 seconds, which is too long for use in
an automobile engine system. When 1 weight
per cent platinum was added as a catalyst the
response time was reduced significantly and in
addition the sensitivity was increased in the
lean-burn region.
Platinum Catalysts in Petroleum Refining

By S. W. Curry, B.S., M.B.A.

Universal Oil Products Company, Des Plaines, Illinois

Reforming processes using platinum catalysts have become of major importance in petroleum refining during the past seven years. They enable the octane rating of naphthas to be greatly increased, and are more economical than any other refining process for the production of high octave gasoline. In this article the general nature of the processes is described and the Platforming process is considered in more detail.

Platinum in any form was virtually unused in the petroleum industry until 1949. Then Universal Oil Products Company introduced it on an unprecedented scale as the active catalytic agent in its Platforming process for catalytically upgrading low octane petroleum naphthas to high quality products.

Prior to the installation of the first UOP Platforming unit, platinum was found chiefly in laboratories in the oil industry. In sharp contrast with 1949, platinum today may be regarded as a most essential item in the production of high octane gasoline for automobiles and piston-engine aircraft. Moreover, substantial portions of the world's benzene, toluene and xylene are extracted from the product obtained by catalytically reforming petroleum naphthas. These chemicals are in large demand as intermediates in the manufacture of many other chemical products such as plastics, man-made fibres, explosives, rubber, insecticides and so forth.

From less than 400 ounces of platinum metal contained in the catalyst charge of that first Platforming unit, the use of platinum by the oil industry—as distinguished from consumption—has climbed to a matter of tons. Thus the oil industry has risen from insignificance to the rank of one of the world’s foremost platinum users in seven years. The end is by no means in sight, since the trend in octane number requirement, particularly for automobiles, has continued to creep upward year by year.

To have advocated the use of 400 ounces of a noble metal, selling at about $70 per ounce at that time, in a catalyst charge for a single small commercial refinery unit, would doubtless have been branded prior to 1949 as impractical idea of a dreamer. UOP’s announcement surprised many in the oil industry for that matter.

Even after the first Platformer had been proven a practical success (it is still operating), it was over a year before the next Platformer was placed in operation. This, of course, is an understandable reflection of the natural prudence of the industry towards any new process. Indeed, while catalytic reforming had first been used as early as 1940, and more units were installed during the early days of World War II, the shortcomings of the non-platinum catalyst and the complexity of the regenerative operation had categorised catalytic reforming in the opinion of the industry as too expensive for the peacetime production of motor and aviation gasolines.

It was nearly two years after Universal’s Platforming process had shown the industry an economically feasible route to high octanes.
and aromatic chemicals from low octane naphthas, that the first competitive processes, also employing platinum-containing catalyst, were brought out by several oil companies and other engineering research organisations. It was 1952 before units employing these processes were ready to run.

There are now six other reforming processes in addition to Platforming available to the industry. All employ platinum-containing catalyst. Universal also has developed a variation on the Platforming process, called "Rexforming", which is in commercial use and employs the Platforming catalysts. Similarly, another licensor offers a variation on his original process. This brings the total of platinum-catalyst reforming processes to nine. (There are five other reforming processes, too, which variously use chromia-alumina, cobalt-molybdena, molybdena-alumina, and bauxite catalysts.) Two processes employing platinum-containing catalysts of undisclosed nature have been announced during 1956 for the isomerisation of C₃ and C₄ hydrocarbons (Universal's "Penex" process and Atlantic Refining Company's "Pentaforming"). No commercial units employing either of them have yet been constructed.

Increase in Octane Rating

The response of the petroleum industry to an economically practicable catalytic reforming process has thus been enormous, since the particular forte of the processes is greatly to increase the octane rating of naphthas over that which can be secured readily and economically by other refinery processes. For a time, non-platinum catalyst reforming processes enjoyed popularity because of the

The Platforming unit at the Kent Refinery of the British Petroleum Company Ltd., on the Isle of Grain. This has a capacity of 6,000 barrels per day.
cheaper catalyst they employ and the relative insensitivity to poisons. This is no longer an advantage because increased by-product hydrogen availability has encouraged refiners to install facilities to clean up contaminated charge stocks, and thus protect the platinum catalyst.

Most of the reforming processes other than Platforming employing platinum catalysts utilise regeneration in situ to prolong catalyst life. Because the catalyst does not require it, Platforming is unique in not employing a separate regeneration system. This is one of the reasons why Platforming requires in general less catalyst per barrel of daily charge capacity than do most of the other processes. But in doing so, however, it suffers no penalty in effective catalyst life, as measured in barrels of charge processed per pound of catalyst employed in the reactor system. Moreover, the higher initial cost and operating complications of regeneration are avoided.

Reactions in Reforming

The numerous reactions comprising catalytic reforming over platinum are complex, interdependent and proceed at different rates. Conditions of temperature, pressure, hydrogen recycle ratio and space velocity therefore are chosen to achieve the optimum overall equilibrium as indicated by the desired octane level (in the case of high octane fuels) or aromatisation (when running for aromatic hydrocarbon production) with a given charge stock.

The reactions may be summed up thus for simplicity:

1. The naphthenes present in the charge are converted to aromatic hydrocarbons by dehydrogenation.
2. Some of the paraffins are isomerised, other paraffins are converted to aromatics, and still other paraffins are hydrocracked.
3. Sulphur compounds which may be present are decomposed to hydrogen sulphide and the corresponding hydrocarbon.
4. Olefins are saturated and then undergo any of the reactions previously mentioned.

The dehydrogenation reaction is particularly energy-consuming and is largely responsible for the decrease in temperature which characterises catalytic reforming. Since the temperature level affects the reaction kinetics and equilibria, heat must be supplied as the reactions proceed.

Because the writer is most familiar with it, the Platforming process is used here to illustrate the commercial catalytic reforming of petroleum naphthas by means of platinum.

The flow diagram above illustrates a typical Platforming process. The raw charge stock is a petroleum naphtha which is prefractionated to separate for the reactor charge a cut boiling
roughly between 200 and 400°F (93 to 204°C) from lower and higher boiling hydrocarbons which may be present. The reactor charge is then mixed with hydrogen generated in the process and heated to the desired reaction temperature, ranging from 850 to 950°F (454 to 510°C). The hot charge is admitted to the first of four (sometimes three) reactors.

Effluent from the first reactor is considerably cooler than when it entered, as a consequence of the endothermic reactions which occur, and is reheated to the operating temperature before it enters the next reactor. This is repeated with the material entering the third and the fourth reactors.

The final effluent is usually heat-exchanged against incoming charge, then further cooled, and finally enters the products separator. Enough hydrogen for process requirements is compressed and recycled to the charge entering the first reactor, while the remainder is by-product hydrogen of high purity. The separator liquid is fractionated to the initial boiling point desired by the refiner, the light hydrocarbons so separated being available for other uses in the refinery.

The illustration on page 39 is an overall view of the Platforming unit installed in the Kent Refinery of The British Petroleum Company Ltd. This has a capacity of 6,000 barrels per stream day. A smaller Platforming unit installed in a refinery in Southwestern United States is shown below, while the figure overpage shows a close-up of the heart of a Platforming unit—the heater and reactor sections. The platinum catalyst is contained in the four cylindrical vessels in the centre of the picture.

**Characteristics of Charge and Product**

The table on page 43 shows the characteristics of the depentanised charge to the reactor section of a Platforming unit and the Platfirmate product. The reactor charge had an octane rating of 48 Research, which probably would have increased to 70 octane or so upon the addition of 3 ml of tetraethyl lead per gallon. This would not be a suitable fuel for a modern automobile. After Platforming, however, the octane number was 93 Research, unleaded, and upon the addition of 3 ml of tetraethyl lead per gallon was rated at over 100 octane. Moreover, the distillation range suits this material for use as an automotive fuel upon the addition of “outside” light
ends to bring the initial boiling point to approximately 100°F and increase the vapour pressure to the range of 9 to 13 pounds. Another important point shown in these data is that a yield of 83.5 per cent C₅⁺ by volume was achieved, despite the very high octane rating secured in the final product and the inherent volume shrinkage which accompanies aromatisation.

Higher octane ratings than are illustrated in the table have been achieved by Platforming. Using the variation called Reforming, which includes solvent extraction to make the desired product, octane ratings of up to nearly 105 Research, leaded, have been reported in commercial operations. Even higher octane ratings can be secured with this process.

World capacity of catalytic reforming units employing platinum-containing catalysts has climbed enormously from the modest 1,500 barrels per stream day represented by the first Platformer. Latest published reports (1, 2) indicate that there are now 1,100,000 barrels per day of platinum-catalyst reforming units in operation in the world, of which nearly 800,000 daily barrels of capacity is in United States refineries. These and other (3) reports show that another 775,000 daily barrels of capacity are either planned or under construction since January 1, 1956. A grand total of 1,885,000 barrels per day of catalytic reforming capacity is thus in sight.

It is a little difficult to estimate how much catalyst or what weight of platinum is represented in these units, since the platinum content of the various catalysts varies with the process and with the type of catalyst within processes. Moreover, there is no uniformity in either the weight of catalyst...
Employed per daily barrel of charge capacity or in the bulk density of the catalyst. Jensen (4) reports that typical catalyst compositions range from 0.3 to 0.8 weight per cent of platinum, and that from three to five pounds of catalyst are required per daily barrel of capacity.

**Variations in Practice**

There are a number of reasons for these variations, among them respective catalyst manufacturing techniques, differences in composition intended to permit the catalyst to be used under various operating conditions, and different processing schemes. One of UOP’s catalysts, for instance, contains more platinum than any of this company’s other catalysts and is tailored particularly for the production of very high octane Platformates. In order to achieve continuity of operations, some regenerative-type processes employ a “swing reactor” which takes the place of that one of the other reactors undergoing regeneration of spent catalyst. Still other processes use more catalyst per barrel of rated capacity in order to extend the time between regenerations, but taking a broad view of the industry it can be said that the amount of platinum embodied in existing reforming installations is measured in hundreds of thousands of ounces, while installations now planned or under construction will absorb further correspondingly large amounts.

The continuing upward trend of octane number requirement for automobile engines shows no sign of ending; there is still a margin of virgin gasoline and naphthas available as reformer feed, while the possibility of widening the range of hydrocarbons economically suitable for feed stocks is being studied. Active expansion of catalytic reforming capacity is therefore probable for some time to come, but a “saturation point” must ultimately be reached after which the building of reforming facilities is likely to slow down and run parallel with the growth of general refining capacity.

### Yield and Properties of Mid-continent Charge and Platformate

<table>
<thead>
<tr>
<th></th>
<th>Naphtha charge</th>
<th>Recovered Platformate</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Yield, volume per cent</strong></td>
<td>100</td>
<td>83.5</td>
</tr>
<tr>
<td><strong>Gravity, °API</strong></td>
<td>55.0</td>
<td>49.0</td>
</tr>
<tr>
<td><strong>Hydrocarbon analysis, volume per cent:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Paraffins</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>Olefins</td>
<td>trace</td>
<td></td>
</tr>
<tr>
<td>Naphthenes</td>
<td>52</td>
<td></td>
</tr>
<tr>
<td>Aromatics</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td><strong>ASTM distillation, °F:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial boiling point</td>
<td>200</td>
<td>110</td>
</tr>
<tr>
<td>10 per cent</td>
<td>222</td>
<td>154</td>
</tr>
<tr>
<td>50</td>
<td>235</td>
<td>180</td>
</tr>
<tr>
<td>90</td>
<td>265</td>
<td>245</td>
</tr>
<tr>
<td><strong>End point</strong></td>
<td>332</td>
<td>336</td>
</tr>
<tr>
<td>364</td>
<td>419</td>
<td></td>
</tr>
<tr>
<td><strong>Sulphur, weight per cent</strong></td>
<td>0.012</td>
<td>Nil</td>
</tr>
<tr>
<td><strong>Reid vapour pressure, lb.</strong></td>
<td>—</td>
<td>4.8</td>
</tr>
<tr>
<td><strong>Research octane ratings:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clear</td>
<td>48</td>
<td>93.0</td>
</tr>
<tr>
<td>Plus 3 ml. octane enhancer</td>
<td>—</td>
<td>100.3</td>
</tr>
</tbody>
</table>

**References**

1. Anon. ... Journal Survey of Refineries in the U.S. *Oil Gas J.*, 1956, 54, Mar. 19, 213-246
3. Courtesy of G. H. Weber ... Prepublication survey estimate, *Oil Gas J.*
Opportunities for Platinum Group Metals in Future Emissions Control Technology

Platinum group metals (pgms) have been a key component in automotive emissions control catalysts and systems since their conception in the first decade of the twentieth century. In 1909 an audience in London was introduced to the idea that a supported platinum catalyst in the exhaust box or silencer could remove the products of incomplete combustion from a gasoline engine (1). This presentation by the French chemist Michel Frenkel, entitled ‘Deodorisation of the Exhaust Gases in Motor Vehicles’, was remarkable as it was only a couple of years after the Model T Ford (Figure 1) went into production.

The Development of Autocatalysts
A century after this first announcement, with the accumulation of over 30 years’ practical experience since the first use of catalysts in the 1970s, commercial catalysts are today applied to most motor vehicles across the globe. There has been a continual striving to improve the catalyst performance and function, but also to reduce, or thrift, the amount of pgms applied to the catalyst. Frenkel suggested 30 g of platinum would be sufficient for the 25 horsepower motor vehicles of his time; today, combinations of platinum, palladium and rhodium are used on much more powerful vehicles. For example, the gasoline three-way catalyst

Fig. 1. Model T Ford © conceptcarz.com
(TWC), which can remove carbon monoxide, hydrocarbons and nitrogen oxides (nitric oxide (NO) and nitrogen dioxide (NO₂), or NOx) simultaneously, contains less than 10 g of pgm and can produce tailpipe exhaust emissions that are cleaner than the air drawn into the engine!

But what of the role of pgms in the future of emissions control? What are likely to be the major challenges?

**The Future of Emissions Control Technology**

An increasing emphasis on greenhouse gas emissions, combined with a need to meet NOx and particulate emissions legislation, means that engine and vehicle manufacturers are forced to improve engine designs and power trains. This means engines will get smaller and new designs will be encountered, for example, hybrids combining an advanced internal combustion engine with a battery (Figure 2). One of the consequences of improved fuel economy is decreasing engine out temperatures. This is often coupled with increased levels of pollutants such as CO, hydrocarbons and particulates. The pgm-containing catalysts of the future will need to be more active, work at lower temperatures, respond rapidly to the change in operating mode of the vehicle, and remove pollutants as soon as the engine is switched on.

For many aftertreatment solutions we are approaching the stage where catalyst performance is not limited purely by catalyst activity. For example, the low temperature performance of a selective catalytic reduction (SCR) catalyst is limited by the temperature at which the urea solution can be injected into the exhaust, and this is governed by urea hydrolysis and the need to avoid the formation of deposits in the exhaust system.

Oxidation catalysts are pgm-based. Their low temperature activity is limited not by activity for CO oxidation but by inhibition by hydrocarbons, NOx and water. Therefore, the use of zeolites to trap hydrocarbons until the catalyst temperature is high enough to burn them will increase. NOx adsorbers, based on pgm, will also be required to hold NOx until the downstream SCR or NOx trap catalysts are warm enough to remove it.

Low exhaust temperatures also pose a problem to components that need periodic regenerations. These include the desulfation of diesel oxidation catalyst (DOC), NOx trap and SCR catalysts and the cleaning of soot from particulate filters. Exhaust systems may require active engineering solutions to modify the exhaust configuration and bypass thermally sensitive catalysts during high temperature regeneration events.

A method that has been practically demonstrated for improving engine efficiency in diesel and gasoline engines is to introduce some hydrogen into the engine alongside the fuel. This helps combustion, and can also reduce emissions of NOx and particulate matter (PM) (2). The hydrogen would be produced by converting some of the fuel into CO, carbon dioxide and hydrogen in a process known as reforming. Typical reformer catalysts will contain pgms, such as rhodium, and to drive the reaction the whole system will need to be integrated with the engine so that waste heat from the engine can be used.

**Emissions Legislation and Fuel Choice**

Worldwide legislation will continue to tighten and encompass new vehicle types and pollutants. For example, in Europe CO₂ emissions regulations will be phased in over the next few years, and nitrous oxide (N₂O), which is 300 times more effective than CO₂ as a greenhouse gas, will be regulated from 2014 in the
USA. Therefore, catalyst chemists and engineers must continue to improve catalysts and systems to produce N₂O in amounts as close to zero as possible. Particulate number will also be controlled in Europe from 2014, and improved systems to control PM will be required in the future as the legislation tightens further. Legislation will also extend to other vehicle types, including ships, trains and stationary engines, and the pgm systems will need to meet the specific challenges of these applications. For example, currently ships use fuel with high sulfur levels, but in-harbour legislation may require them to carry low sulfur fuels for use in port. Also, stationary engines can be very large, and therefore so will be the catalyst which, if pgms are needed, necessitates very efficient use of the pgm to bring the cost as low as possible.

Another future challenge for emissions control catalysts could be the range of fuels available. It is already possible to buy many of the ‘new’ fuels, and it will be necessary for the catalysts to work no matter what fuel is used in the engine; some new vehicles and ships already use dual fuel engines. Fuels that may be encountered include synthetic fuels, such as those derived from coal or biomass; hydrogen; biofuels such as fatty acid methylesters or ethanol; methanol; compressed natural gas; and blends of these.

Conclusion

Lower temperatures and the continuing presence of poisons will continue to restrict the use of base metal catalysts and necessitate the use of pgm catalysts. But even in the event that base metal catalysts find a greater role in emissions control technologies, for example in SCR catalysts, these are significantly promoted by upstream pgm catalysts for NO₂ generation. Thrifting of the pgms will continue to be important while the catalysts still need to operate efficiently and overcome all the challenges outlined. To address all these issues an integrated approach is required, involving fuel suppliers, engine and vehicle manufacturers, and catalyst chemists and technologists. Without a doubt, with all these new challenges, many opportunities for pgm-containing emissions control catalysts and adsorbers remain as we look to the future.

*This article is based on and updated from an item written for the Royal Society of Chemistry’s journal Education in Chemistry (3).*

PAUL J. MILLINGTON AND ANDREW P. E. YORK*

Johnson Matthey Technology Centre, Blounts Court, Sonning Common, Reading RG4 9NH, UK

*Email: ayork@matthey.com

References


The Authors

Dr Paul Millington originally joined Johnson Matthey in the Emission Control Research group in 1995. After a short break in the automotive industry he rejoined in 2001. He currently works on all forms of pgm-containing aftertreatment in the Emission Control Research group at the Johnson Matthey Technology Centre, Sonning Common.

Dr Andy York joined Johnson Matthey in 2000, initially in the Emission Control Research group, he is currently on secondment at the Department of Chemical Engineering and Biotechnology at the University of Cambridge working on a range of academic and business related projects involving catalysis and engineering.
Platinum in Next-Generation Materials for Data Storage

Introduction

Magnetic memory in the form of hard disks has been in use in the computer industry since the first hard disk system was commercially released by IBM in 1956. That first system stored 2000 bits of data per square inch, equivalent to about 5 MB in total on 50 separate 24-inch diameter disks (1, 2), but data storage capacity grew exponentially throughout the latter half of the twentieth century, in tandem with – and sometimes outstripping – growth in processing power (3, 4).

The capacity of a hard disk system depends on many factors, but is fundamentally dictated by how much information the magnetic medium can hold (3, 5). This can be quantified using areal density: the number of bits per unit of surface area, currently quoted in gigabits per square inch (Gb in$^{-2}$). For magnetic memory to keep pace with developments in the computer industry and see off challenges from competing solid-state memory technologies, areal densities must continue to grow rapidly. The next frontier in storage capacity will see density values of commercial systems of the order of terabits per square inch (Tb in$^{-2}$). However, significant technological innovation will be necessary to bring this about (3, 4).

Much of this innovation will centre on the magnetic medium: how it is structured and what materials are used. Existing media contain platinum (Figure 1) and, more recently, ruthenium (6, 7). These metals offer a number of advantages in the magnetic storage of data and they have played an integral part in delivering the growth in areal density seen to date (2, 8–10). Demand for both in this application is significant, amounting to over 95,000 oz of platinum and over 50,000 oz of ruthenium in 2009 (6). It is therefore worth considering what role the platinum group metals (pgms) will play in increasing storage capacity into the future.

In fact, the pgms feature prominently in new materials currently under research (3). This article has selected one example of a platinum-based material as illustration of this, with two contrasting approaches highlighted. This is intended to give a flavour for the challenges facing the pursuit of higher areal densities and the novel ways in which these may be overcome.

The Limitations to Areal Density

Magnetic recording exploits the phenomenon of ferromagnetism. Ferromagnetic materials align with an applied magnetic field and retain much of this alignment as remnant magnetism after the external field has been removed; in other words they exhibit bulk anisotropy. In a granular ferromagnetic medium, data can therefore be encoded in the spatial orientation of the remnant magnetic fields of successive groups of grains, with each group then constituting one bit. The information is held in the transition from one bit to the next; the head will return a ‘1’ or ‘0’ depending on whether or not it picks up a change in direction (3).
Clearly, density is increased by reducing bit size and allowing more bits to be packed in per square inch. Bit size can be reduced in two ways: by including fewer grains per bit and by making the grains themselves smaller. This is by no means straightforward and in practice has to be weighed against other performance parameters. The persistence and integrity of the data recorded in the magnetic medium is of particular importance: the bit configuration should be stable, ideally for five years or more, and the signal output from the bits should degrade only minimally (2). These factors place stringent requirements on the medium that limit the extent to which bits can be downsized (4, 11).

The first requirement is an acceptable signal-to-noise ratio (SNR). In conventional granular media, grains are irregular in shape, size and arrangement. In addition, the magnetic fields of grains in adjacent bits may become coupled so that they do not align independently. These imperfections give rise to noise in the data and therefore each bit must consist of a number of grains sufficient for the average to be used as a distinguishable signal (2, 3, 11).

The second requirement is that the medium be thermally stable. For a given material, the smaller the grains are, the lower their energy barrier to magnetisation reversal – making it more likely that the data will be disrupted by thermal variations in the environment. Each ferromagnetic material is therefore subject to a lower limit for grain size below which data cannot be stably encoded: the superparamagnetic limit (11).

The recent introduction of perpendicular magnetic recording (PMR) facilitated improvements in both SNR and data stability by changing the orientation of the bits in the plane of the medium and adding a soft underlayer to enhance the write field (3, 11–13) (Figure 2). As a result PMR has allowed continued growth in data storage capacity, beyond what was thought achievable with conventional thin-film media. However, existing PMR media are not a complete departure from these conventional media and are still subject to the above-mentioned constraints limiting eventual reduction of bit size. Therefore, although the limit to areal density has been greatly deferred, it still exists. It is generally considered that to achieve densities much beyond 1 Tb in$^{-2}$ new materials will be necessary (3, 4).

**Shrinking Bits**

In the light of this, there are various approaches to be taken in developing media with reduced bit size.

In the first instance, fewer grains would be necessary per bit if the medium were more regular with distinct transitions between bits. In the ideal case, bit shape and size would be consistent and the bits would be arranged in uniform arrays. There are a number of strategies currently being explored to improve regularity in magnetic media, with the concept of patterned media receiving particular attention (2–4), notably from Hitachi Global Storage Technologies, Ltd (Figure 3) (13).

Bits can also be made smaller if the superparamagnetic limit to grain size is lowered. The energy

---

**Fig. 2. Comparison of conventional (longitudinal) and perpendicular magnetic recording (PMR) modes.** PMR enables higher density by orientating the bits perpendicular to the disk, reducing repelling forces between bits and allowing higher head fields (13). The recording layer in each typically contains platinum. Reprinted from (13) with permission from the authors and Hitachi, Ltd.

---
barrier of a grain in the absence of an external field, $E_0^0$, is given by $K_u V$, where $V$ is the volume of the grain and $K_u$ is the magnetic anisotropy constant (giving the magnetic anisotropy energy per unit volume) (3). Hence, to maintain the energy barrier while decreasing grain size, material with a higher anisotropy constant must be used. The medium then possesses a higher coercivity, $H_c$, a measure of the intensity of the magnetic field which must be applied to remove all the remnant magnetism of the material and a good indicator of data stability. This also means that a more intense field is required to write, and overwrite, the data. As materials with very high anisotropy energy come into use, this may prove problematic due to practical restrictions on the magnetic field of the head. The problem is not insurmountable and is the focus of much research and development, particularly into methods of microwave-assisted magnetic recording (MAMR) or heat-assisted magnetic recording (HAMR), in which the head carries an energy source to locally heat each bit as it is written, temporarily lowering the coercivity. After writing, the bit is then quenched and returns to high coercivity so that the information is stabilised (2, 4, 14).

**Iron-Platinum Nanoparticles**

Novel materials with large values of $K_u$ and which can be used in a highly regular form are thus being sought. Iron-platinum alloys of approximately equimolar composition are known to have high $K_u$ values, specifically in the ordered tetragonal L1$_0$ phase (3). Furthermore, it is possible to form L1$_0$ FePt nanoparticles of very small size (around 3 nm) with a high degree of chemical stability (15, 16).

The use of nanoparticles in recording media has been proposed as an extension of the concept of patterned media. Patterned media consist of arrays of magnetic islands arranged in a nonmagnetic matrix. The grains within one bit (or island) are exchange coupled and act in concert, while being completely decoupled and independent from surrounding bits. Bit transitions are thus sharp, and the averaging required in conventional granular media is not necessary. However, ultrahigh densities (10 Tbit $\cdot$ in$^{-2}$ or more) will most likely not be achieved using current nanofabrication techniques such as lithography as it becomes increasingly difficult to manufacture structures on the very small scales required (2, 3). Nanoparticles, while potentially offering the same advantages as bit-patterned media, are generated by chemical synthesis and form arrays through self-assembly, allowing smaller sizes to be obtained and facilitating regular arrangement on a substrate. Equally importantly, nanoparticles tend to be monodisperse. Variation in size can be limited to below 5% (15), compared with 20–30% in granular media (17).

**Fig. 3.** Patterned media replace the many random grains of conventional, continuous thin-film media with one large magnetic island that stores a single bit. The bits can then be scaled to smaller size, allowing higher density while remaining thermally stable. Reprinted from (13) with permission from the authors and Hitachi, Ltd.
FePt nanoparticles would therefore fulfil both the requirement for high anisotropy energy and the need for uniformity. However, there are a number of problems with the use of FePt nanoparticles which must be overcome to make them viable for magnetic recording.

Nanocubes
A patent from Seagate Technology LLC in the USA, one of the leaders in this field, reports progress on this front (18). It addresses two concerns: firstly, the fact that it is difficult to align the magnetic axes of spherical FePt nanoparticles once deposited on a surface and, secondly, that they produce a relatively small magnetic signal. The inventors claim a method for producing nearly cubic or rectangular FePt nanoparticles, 4–10 nm in size, which have their facets parallel to the (001) crystallographic plane (Figure 4)(19). During deposition onto a substrate, cubes will assume greater regularity than spheres simply because to be stable the cubes must have one facet flat on the plane and therefore parallel to it. The cubic nanoparticles are found to arrange themselves with their [100] axes perpendicular to the surface, and their [010] and [001] axes parallel to it and aligned locally with each other in square arrays. In addition, these cubic nanoparticles produce a larger signal than spherical particles of similar dimensions. This is because signal strength depends on the magnetic thickness of the medium, and magnetic thickness of nanoparticles has been shown to be a function of their geometry: square is better (18).

There is, however, a potentially more serious limitation which this patent claims to have made only partial progress towards solving. Typically, Fe-Pt nanoparticles are produced via synthesis methods that form a magnetically soft face-centred cubic (fcc) crystal structure. Annealing is then necessary to transform the structure to the magnetically hard face-centred tetragonal (fct) phase (2, 16). The drawback with heat treatment after synthesis is that it may lead to undesirable particle aggregation and magnetic coupling – precisely what patterned media are designed to prevent. The higher-temperature synthesis technique proposed in this patent does appear to induce some phase transformation from fcc to fct during formation of the particles, but it is likely that further annealing will be necessary.

The inventors do not address in this patent the issue of how to write data in a medium which is so magnetically hard that the required switching field is beyond the intensities achievable with existing head technology. However, it can be assumed that this patent forms part of a strategy that Seagate has previously publicised: the use of HAMR in combination with FePt nanoparticles (20).

Capped Nanoparticles
A European research group may have found a way to harness the advantages of both FePt alloy and nanoparticles, without the attendant disadvantages described above. The proof of concept was carried out in the MAFIN project (for ‘magnetic films on nanospheres: innovative concept for storage media’), which was funded under the EU’s Sixth Framework Programme (21, 22). Instead of nanoparticles composed of ferromagnetic material, the group used silica nanospheres with a thin layer of the magnetic medium deposited as a cap. Initially, researchers looked into using multilayers of cobalt/platinum or cobalt/palladium as the magnetic medium (17, 23, 24) but in this project the focus moved to FePt as a promising material (21).

If the deposition is done correctly, the spherical shape of the silica particles causes the magnetic film to form uniform, decoupled islands. Deposition of the film can be controlled to impart perpendicular anisotropy to the islands, or a ‘tilted’ medium can be created (Figure 5 (a)). Coercivity depends on the angle between the switching field and the magnetic easy axis of the particle. By tilting the medium, materials with a high $K_u$ can be made more easily writable (17, 24).
As the nanoparticles are not themselves magnetic, they can be arranged adjacent to and in contact with each other in closely packed arrays (Figure 5 (b)). The nanospheres are ∼25 nm in diameter and if they are packed tightly, a storage density of 1 Tb in $^{-2}$ should be possible. A successor project (TERAMAGSTOR for ‘terabit magnetic storage technologies’) is aiming to produce smaller spheres and higher densities (25). The research group has also proposed a novel way to write and read the FePt bits, using a fine probe with a magnetic tip (21).

**Concluding Remarks**

Ten years into the 21st century, data storage is still dominated by magnetic memory, particularly in the form of hard disk drives (HDDs) (26). While portable devices, and even some desktop PCs, are now using solid-state drives (SSDs), their cost-per-GB of capacity remains at least an order of magnitude higher than that of HDDs (27, 28). This is likely to be the case for some years yet. Of more immediate concern, perhaps, are the demands placed on the technology by the need for ever-increasing storage capacities. While the limits of existing materials are approaching, many new materials now in development are poised to deliver step-changes in areal density growth.

The pgms have featured in many major developments in magnetic data storage, of which perpendicular magnetic recording is the most recent example, and they look set to continue doing so. Just two examples of applied research into pgm-based materials have been discussed here, but there are many more. It is quite possible that the platinum group metals may once again prove to be key in realising the standard medium for HDDs of the future.

---

**References**


---

© 2010 Johnson Matthey

---

![Figure 5](image-url)


Platinum Catalysts Used in the Silicones Industry

THEIR SYNTHESIS AND ACTIVITY IN HYDROSILYLATION

By Larry N. Lewis, Judith Stein, Yan Gao, Robert E. Colborn and Gudrun Hutchins

GE Corporate Research & Development Center, General Electric Company, Schenectady, New York

Hydrosilylation is a reaction widely used in the silicones industry for the preparation of monomers, containing silicon-carbon bonds, and for crosslinking polymers, and results in a variety of products. Hydrosilylation reactions are catalysed by highly active platinum catalysts, such as the silicate-soluble Karstedt's catalyst, which is prepared by the reaction of chloroplatinic acid, \( \text{H}_2\text{PtCl}_6 \), with vinyl-silicon containing compounds, such as divinyltetramethyl disiloxane, \( \text{M}^1\text{M}^1 \). Inhibitors are widely used during hydrosilylation reactions to prevent premature crosslinking of polymers at ambient temperature, but permit rapid platinum-mediated crosslinking reactions at higher temperatures. Platinum colloids are formed at the end of the reaction and were identified by analysis. This paper discusses the mechanism of the hydrosilylation reaction, catalyst formation, characterisation, the effects of inhibitors and the range and complexity of the end products.

The silicones industry extensively uses the platinum-catalysed hydrosilylation reaction, in which a silicon-hydrogen (Si-H) bond is added across the unsaturated carbon-carbon double bond (C=C) of an olefin, Equation (i), resulting in the formation of a silicon-carbon (Si-C) bond (1–8).

\[ \text{R}_3\text{SiH} + \text{H}_2\text{C} = \text{CHR} \rightarrow \text{R}_3\text{SiCH} = \text{CHR} \quad \text{(i)} \]

Hydrosilylation can be used for the synthesis of monomers; for example, in Equation (ii) the addition of a methyl dichlorosilane to an alkene gives a monomer, a methylidichlorosilyl-substituted compound, which upon hydrolysis gives a polymer, a polysiloxane with hydrocarbon functional groups.

Hydrosilylation is used to a much greater extent in industry to produce crosslinking reactions (9–11). The crosslinked network shown in Equation (iii), for example, is created by the addition of platinum to a mixture composed of a difunctional vinyl-containing polydimethylsiloxane and the multifunctional Si-H-containing copolymer of polydimethylsiloxane and methylhydrogen siloxane.

Here, to show the crosslinking in the polymer

![Diagram of the crosslinking process](image)

\[ \text{(ii)} \]
chain which has been catalysed by platinum, the M, D, T and Q notation is used, where M, D, T and Q refer to mono, di, tri and quaternary oxygen substitution at silicon and where a superscript is used to describe substitution at silicon other than methyl as in "M" which refers to vinylidimethylsiloxane, D is dimethylsiloxane and D" is methylhydrogen siloxane.

Crosslinked siloxanes such as these are used for: automotive gaskets, paper release coatings, pressure sensitive adhesives, baby bottle teats, and many other applications. So-called liquid injection molding (LIM) applications employ hydrogellation for curing and LIM finds application in computer key pads, to name just one current use.

Hydrosilylation Catalysts

One class of platinum compounds used as hydrosilation catalysts are Pt(0) complexes containing vinyl-siloxane ligands (12, 13). An example of such a catalyst is Karstedt's catalyst, Pt6(M"M")3, formed by the reaction of divinyltetramethylsiloxane (M"M") with chloroplatinic acid, H2PtCl6, Equation (iv).

\[
\text{iv) } \text{Pt6}(\text{M"M"})_3 + 6\text{H}_2\text{PtCl}_6 \rightarrow 6\text{H}_2\text{PtCl}_6 + 6\text{M"M"} + \text{Pt6Cl}_6
\]

Karstedt's catalyst is a Pt(0) complex which contains both bridging and chelating di-vinyl ligands (14, 15). The designation of Pt6(M"M")3, and M"D"M" as "solution A" is taken from the work of Lappert's group and is used to describe the mixture of products containing platinum and vinyl-siloxane oligomers (16, 17).

In the late 1960s and early 1970s, Willing of Dow Corning (18) and Karstedt of GE (15) described the reaction of chloroplatinic acid and vinyl-containing siloxane monomers to make silicone-soluble platinum complexes.

Little was then known (19) about the structure of the platinum complexes which resulted from the reaction shown in Equation (iv) until the work of Lappert and co-workers (16, 17). The Lappert group reported that the platinum product, 1, of Equation (v):

\[
2\text{Pt(COD)}_2 + 3\text{M"M"} \rightarrow \text{Pt}6\text{(M"M")}_3
\]

The COD = 1,5-cyclooctadiene

contained a bridging M"M" and each platinum had a chelating M"M" group. 19Pt NMR spectroscopic analysis of "solution A" showed the presence of two resonances which Lappert suggested was due to two isomers of 1. We proposed that the two 19Pt NMR resonances were caused by the presence of 1 and 2, see Equation (vi) (20).

\[
\text{vi) } 2\text{Pt(M"M")}, \xrightarrow{1:1} \text{Pt}(\text{M"M")}_3 + \text{M"M"} + \text{M"M"}
\]

When "solution A" was combined with vinyl-stopped polydimethylsiloxane oligomers, a single 19Pt resonance was observed. Furthermore,
analysis of "solution A" by field desorption mass spectroscopy (FDMS) showed the presence of 2 and vinyl-stopped oligomers, as shown in Equation (iv).

The reduction of Pt(IV) to Pt(0) by a silicon-vinyl group, in Equation (iv), appeared to be a new reaction. When M"M' was the reducing agent, some of the silicon vinyl functionality was converted to a silicon-oxygen group. The net result was the conversion of an M" group into a D (dimethylsiloxane) group. The vinyl group was changed primarily into either butadiene or ethylene. Water was the source of the new oxygen bond to silicon. Similarly, when D' is the source of reducing agent, as in the reaction of Equation (vii), a D' group is converted into a T group.

The overall platinum conversion occurring in Equation (iv), is from Pt(IV) to Pt(0); the platinum in "solution A" being in the zero oxidation state. We attempted to observe the imputed Pt(II) intermediate from this vinyl-silicon-mediated reduction in Equation (iv). Typically, in this reaction, chloroplatinic acid is reacted with M"M' in the presence of some ethanol, which aids in the dissolution of H₃PtCl₆. Sodium bicarbonate was added to remove chloride. Both ethanol and NaHCO₃ may aid the reduction. A ¹⁹⁵Pt NMR spectrum of "solution A" showed the previously mentioned resonances at ~6200 ppm.

However, when the reduction was carried out without ethanol or NaHCO₃, a broad ¹⁹⁵Pt resonance was observed at ~3470 ppm, which may be due to a Pt(II) intermediate. In order to characterize further the potential Pt(II) intermediates and to improve understanding of the mechanism of the reduction process, H₃PtCl₆ was reacted with several silicon-vinyl-containing species. The product of the reaction of H₃PtCl₆ and dimethylvinylsilane, (CH₃)₂Si(=CH₂)₂ gave two products, see Equation (viii), a Pt(II) complex, 3, and a Pt(0) structure, 4. Complex 3 was isolated and a single crystal X-ray structure, see Figure 1, showed it to be a di-nuclear complex with two bridging chlorine atoms and a bridging (CH₃)₂Si(=CH₂)₂ ligand. Additionally each platinum atom in 3 contained a η¹:η¹-(CH₃)₂Si(=CH₂)(CH₃CH₂) ligand. Compound 3 had a ¹⁹⁵Pt NMR resonance at ~3603 ppm, while the Pt(0) product, 4, had a ¹⁹⁵Pt NMR resonance at ~6152 ppm. Although the structure of 4 was not determined directly, addition of PPh₃ to solutions containing 4 produced (M"M')₃Pt(PPh₃) suggesting that 4 was Pt₃(M"M')(CH₃)₂Si(=CH₂)₂, (20).

Inhibitors

Another important aspect of industrial hydrosilylation is the use of inhibitors (21–23). The crosslinking reaction of Equation (iii) will usually occur with as little as 10 ppm platinum, at ambient temperature in a matter of minutes. The rapidity of this reaction leads to the need...
for inhibitors to give some control over the reaction. Typical industrial applications require long work times at low temperatures, followed by fast curing times at elevated temperature.

Two inhibitors, dimethyl fumarate and dimethyl maleate, are commonly added to platinum-catalysed crosslinkable silicone formulations to permit long work life by the end user at ambient temperature with a rapid cure at elevated temperature. The reaction of "solution A" with four equivalents of dimethyl fumarate, relative to platinum, resulted in formation of a platinum-fumarate complex, 5, see Equation (ix). Complex 5 was characterised on the basis of its $^1$H NMR spectrum and by comparison of its spectrum with those of the maleate analog, 6, and the previously well characterised compound PPh$_3$Pt(M"M")$_2$, 7. Compound 7 was prepared by the reaction of "solution A" with one equivalent of PPh$_3$, in the presence of 10 equivalents of M"M". In effect the fumarate (or maleate) replaces the bridging, but not the chelating
M"M" ligand in Karstedt's catalyst.

A comparison of the "C NMR spectra for 5, 6 and 7 in the olefin-platinum region is shown in Figure 2. All the "C olefin resonances had "Pt satellites. The spectrum of 5 showed four overlapping triplets from 68 to 72 ppm. These four resonances derived from the four different olefinic carbons present in the chelating M"M" ligand.

By contrast, the "C NMR spectrum for 6 had two resonances for the olefinic carbons of the M"M" ligand because the two double bonds are chemically equivalent. The downfield triplet resonance at 69.2 ppm (J(CC) = 56 Hz) was assigned to the methylene carbon of the M"M" ligand of 6, while the methyne carbon was the triplet upfield at 71.94 ppm (J(CC) = 42 Hz). Both 5 and 6 showed peaks in the "C NMR due to the olefinic carbons of fumarate and maleate, respectively, with large coupling constants: J(CC) = 89 and 104 Hz, respectively. Compound 7, where maleate or fumarate was replaced with PPh3, had two resonances for those of the olefinic carbons of M"M", but shifted upfield relative to those in 6 due to the presence of the PPh3 ligand.

Platinum Colloid Formation

The mechanism of the hydroisilylation reaction at the molecular level has been studied for many years (1-8), and several reviews have been devoted to the reaction (24-28). The Chalk-Harrod mechanism, developed during the 1960s, is the most often cited mechanism for hydroisilylation and is based on fundamental steps of organometallic chemistry (8); these include oxidative addition of a Si-H group to a metal-olefin complex, insertion steps and reductive elimination. However, a number of
phenomena are not explained by the Chalk-Harrod mechanism and among these is the presence of an induction period (the time between the start of a chemical reaction and its observable occurrence), formation of coloured bodies and co-catalysis by oxygen.

In the 1980s Lewis and co-workers proposed a mechanism based on the intermediacy of platinum colloids (13, 14, 25, 26), which had been observed via transmission electron microscopic (TEM) analysis of reaction solutions following platinum-catalysed hydroxylation (27).

Reaction solutions from a platinum-catalysed hydroxylation reaction were originally analysed by first evaporating the reaction solutions and then recording the TEM images (12–14, 22–25). TEM analysis showed, in some cases, that colloidal platinum had formed after the hydroxylation reaction. More recently, Pt EXAFS of reaction solutions from hydroxylation reactions has shown that the type of platinum species formed in solution at the end of a reaction depends on:

* the ratio of Si-H to vinyl used (21), and
* the nature of the olefin (hydrocarbon or silicon-vinyl).

The two types of platinum end products observed are illustrated in Equation (x) where

\[ \text{SiH} + \text{SiH} \xrightarrow{\text{Korsteidt catalyst}} \text{SiH-vinyl} \]

\[ \text{SiH} + \text{SiH} \xrightarrow{\text{Korsteidt catalyst}} \text{SiH-vinyl} \]

or equal to, that of vinyl. Compound 8 was the designation used for platinum species containing only Pt-C bonds (at a typical Pt-C:olefin distance of around 2.17 Å and with a co-ordination number, number in parentheses, of six). Compound 9 was the species that contained both Pt-Pt and Pt-Si single bonds as determined by EXAFS.

Platinum species 9 could be converted to 8 in the presence of excess olefin (if the olefin was a silicon-vinyl compound, that is, if more MD3'M was added). Compound 8 was formed when silicon-olefin was the olefin source, that is, MD3'M.

However, if a Si-H compound was reacted with an olefinic hydrocarbon, such as hexene, which does not contain silicon-vinyl, then 9 was formed regardless of the stoichiometry of olefin and Si-H. Similarly, with neo-hexene (3,3-dimethyl-1-hexene) platinum reaction product 9 is formed from the platinum-catalysed hydroxylation reaction between neo-hexene and a number of different Si-H compounds, even if the concentration of Si-H:neo-hexene is 1:2.

The reactions in Equations (xi) to (xiv), where

\[ \text{SiH} + \text{Pt} \xrightarrow{\text{evaporation}} \text{Pt} + \text{SiH-vinyl} \]

(xi)

\[ \text{SiH} + \text{Pt} \xrightarrow{\text{evaporation}} \text{Pt} + \text{SiH-vinyl} \]

(xii)

\[ \text{SiH} + \text{Pt} \xrightarrow{\text{evaporation}} \text{Pt} + \text{SiH-vinyl} \]

(xiii)

\[ \text{SiH} + \text{Pt} \xrightarrow{\text{evaporation}} \text{Pt} + \text{SiH-vinyl} \]

(xiv)

Note that D3 is cyclooctamethytrisiloxane.
solutions after evaporation all show that platinum crystallites were present.

A representative TEM, from Equation (xiii), is shown in Figure 3; here individual crystallites can be seen, displaying diffraction fringes with spacing which matches that for the (111) plane in crystalline platinum. The diffraction pattern also could be indexed to that of platinum. Finally, energy dispersive X-ray spectroscopy of the spots confirmed that they were composed of platinum.

In the reactions shown in Equations (xi) and (xii), in situ studies showed that platinum of type 9 (from Equation (xi)) formed in the reactions with neo-hexene. On evaporation, the type 9 platinum composition is converted to platinum crystallites. The effect of dilution with D, or of running the reaction without solvent was examined together with the effect on platinum crystallite size. Reactions between dimethylsiloxysilane and either Karstedt’s catalyst (Equation (xii)) or PtCl₂ (Equation (xiv) (12)) were carried out under conditions where previous reports had shown that colloids formed. The Table shows the results of a statistical analysis of the particle sizes of the platinum crystallites formed from the reactions in Equations (xi) to (xiv).

The particle size of the crystallites may have been affected by the platinum concentration; it can be seen in the Table that the larger particles from Equation (xiv) are produced from a higher platinum concentration. The particles formed from Equations (xi) and (xii) were

| Statistics on Particle Sizes of Platinum Crystallites Formed in Equations (xi) to (xiv) |
|-----------------------------------|---------------------------|---------------|-----------------|---------------|
| Equation | Pt concentration, mg ml⁻¹ | Mean, Å | Minimum, Å | Maximum, Å | Standard deviation |
| (xi)     | 0.29                      | 24.4     | 16          | 36.1         | 3.6           |
| (xii)    | 0.3                       | 17.3     | 10.3        | 26.4         | 3.9           |
| (xii)    | 0.3                       | 22.6     | 9.6         | 33.3         | 3.6           |
| (xiv)    | 0.48                      | 30.4     | 17.6        | 46.9         | 5.4           |

Platinum Metals Rev., 1997, 41, (2)
similar in size and larger than those from Equation (xii). Equation (xii) did not use D, diluent.

When hydrosilylation reactions were run with silicon-vinyl substrates, for example Equation (x) where platinum of type 8 is formed, TEM analyses of the resulting evaporated solutions were different from those obtained from Equations (xi) to (xiv). Note that all of these reactions were carried out in neat solutions and it is not known if the absence of diluent contributed to the observed TEM. TEM of evaporated solutions from Equations (xv) to (xviii) showed the complete absence of the platinum crystallites seen in Figure 3.

\[
\begin{align*}
M'\text{M} + M'\text{M} & \xrightarrow{\text{Pt}_2} \quad \text{(xv)} \\
M'\text{M} + M''\text{M} & \xrightarrow{\text{Pt}_2} \quad \text{(xvi)} \\
M'\text{D} + M'\text{D} & \xrightarrow{\text{Pt}_2} \quad \text{(xvii)} \\
M'\text{M} + (\text{CH}_2\text{CH}_2)\text{SiH}_3 & \xrightarrow{\text{Pt}_2} \quad \text{(xviii)}
\end{align*}
\]

A darkfield TEM micrograph, prototypical for the evaporated solution from Equations (xv) to (xviii) is shown in Figure 4. Energy dispersive X-ray spectroscopy confirmed the presence of platinum. However, the diffraction pattern did not match that of metallic platinum or any platinum compound in the powder diffraction file. Electron diffraction analysis indicated the presence of a crystalline material which had formed in very thin crystalline sheets that were slightly misaligned with respect to one another. The moiré diffraction fringes due to this misalignment are clearly visible in the micrograph.

Evaporation of the product solution from the reaction between PtCl₄ and a siloxane-like Si-H source, M:TM'H, tris(trimethylsiloxy)silane (Me₃SiO)₃SiH, gave a TEM similar to Figure 3, while evaporation of the product solution from the reaction between PtCl₄, M:TM'H and M:TM'H gave a TEM similar to Figure 4. Further studies are underway to determine the structure of platinum species present during hydrosilylation under the various conditions discussed here. The species in Figure 4 may be explained by these analyses (29).

**Summary and Conclusions**

Hydrosilylation is widely used industrially for the preparation of monomers with silicon-carbon bonds and for producing crosslinked polymers.

Highly active, silicone-soluble platinum catalysts can be prepared by the reaction of chloroplatinic acid with vinyl-silicon containing compounds. The vinyl-silicon compounds, such as
divinyltetramethyldisiloxane (M"M") reduce platinum (IV), in chloroplatinic acid, to platinum(0) with the concurrent conversion of the silicon-vinyl group to a silicon-oxygen group. A typical platinum catalyst is Karstedt's catalyst, Pt(M"M").

Inhibitors are widely used in industry to control the platinum-mediated addition reaction of curable systems. The addition of inhibitors prevents hydroisolation (crosslinking) at low temperature while permitting rapid reaction at elevated temperature. Commonly used inhibitors include those with electron deficient double bonds, such as maleates and fumarates. Dimethyl maleate reacts with Karstedt's catalyst to make a complex containing a chelating M"M" group and a maleate ligand.

Previous studies reported that formation of platinum colloids was a key step in hydroisolation. It is now clear that colloid formation occurs as an end stage of the reaction. EXAFS analysis has shown that molecular compounds are present during hydroisolation. Colloidal platinum is observed by TEM after evaporation of solutions from several reactions which involve platinum, a Si-H compound and either poorly co-ordinating olefins or no olefin. However, in some cases where silicon-vinyl-containing species were present, the reaction product between platinum and a Si-H-containing compound did not give colloidal platinum species; and TEM analysis showed that the crystalline material present was not metallic platinum crystallites.

Further work is in progress to identify the structures of platinum intermediates formed during hydroisolation and industry continues to search for more highly active catalysts and more effective inhibitors.

Acknowledgements

I would like to thank Jim Grande for performing the statistical analysis from the TEM images.

References

13. L. N. Lewis and R. J. Uriarte, Organometallics, 1990, 9, 621
15. B. D. Karstedt, U.S. Patent 3,775,452; 1973
New Platinum-Based Lean NOx Conversion Strategy

The introduction of increasingly stringent environmental legislation brings benefits to our quality of life, and presents challenges to catalytic chemists, who are required to develop novel solutions to enable the new legislation to be met. Within the automotive area, new legislative limits to exhaust pollutants mean that it will soon be necessary for the catalytic converters on diesel vehicles to additionally remove significant concentrations of nitrogen oxides, NOx, from the exhaust feed, besides the oxidation functions for carbon monoxide, CO, and hydrocarbon which they already perform.

Diesel engines are extremely fuel-efficient. This is achieved by ensuring that combustion occurs under highly oxidising conditions, and results in a strongly oxidising gas feed which needs to be treated using a catalytic converter. Under such highly oxidising conditions the oxidation of the unburnt hydrocarbons to CO and H2O and of the CO to CO2 is relatively straightforward. However, reducing NOx to N2 under such conditions is very difficult.

The major breakthrough in automotive NOx control under very oxidising conditions was reported simultaneously by the Held group in Germany (1) and by the Iwamoto group in Japan (2). These workers independently showed that significant quantities of NOx could be reduced to N2 under highly oxidising conditions using a catalyst of copper incorporated into ZSM-5 zeolite. Others have characterised the mechanisms of the reaction over Cu/ZSM-5 (for example (3)), and have shown that the major role of the copper is to oxidise NO to NO2. This subsequently reacts with hydrocarbon-derived species activated by the surface of the zeolite.

The copper catalyst can only be used at relatively high temperature (350–550°C), and it is not particularly stable. The conversion of NO to NO2 over copper is poor at the low temperature end of this range, so its performance here is nowhere near as good as that of platinum. At high temperature the NO to NO2 reaction becomes limited by thermodynamics and both copper and platinum catalysts then become equivalent in their NO oxidation performance.

Now, Iwamoto has used the mechanistic information/ approach to develop a highly efficient NOx conversion catalyst system capable of operating at low temperatures (4). The strategy uses two separate catalysts—one to oxidise the NO into NO2 and the other to reduce this NO2 into N2. Iwamoto has shown that platinum incorporated into ZSM-5 zeolite is a highly efficient NO oxidation catalyst and this catalyst is used to perform the first step in the conversion process. The second step is carried out using indium incorporated into ZSM-5 zeolite. Since there is only a small amount of unburnt hydrocarbon in the exhaust stream of a diesel vehicle, additional hydrocarbon needs to be injected to provide the reactant to achieve significant NOx conversions.

Position of Hydrocarbon Injection

Platinum is an excellent oxidation catalyst, which means that if the hydrocarbon were injected in front of the platinum catalyst, substantial quantities would be converted over the platinum, thereby lowering the hydrocarbon concentration reaching the indium catalyst. Iwamoto proposes that this additional hydrocarbon injection should instead occur between the two catalysts: that is, after the platinum catalyst and before the indium catalyst, thus ensuring that the indium reduction catalyst sees enough hydrocarbon to effect the reduction of the NO2 generated over the platinum catalyst. This approach is the latest in the long line of platinum-based strategies developed to remove NOx under highly oxidising conditions. Within industry and academia, platinum-based work is continuing to advance the technology further to ensure that future environmental legislation can be met.

References

Some Biological Effects of Platinum Compounds

NEW AGENTS FOR THE CONTROL OF TUMOURS

By Barnett Rosenberg
Department of Biophysics, Michigan State University

Certain complexes of the platinum group metals exhibit interesting biological effects. At low concentrations some are effective bacteriocides; others stop cell division and force bacteria to grow into long filaments. These complexes can also induce destruction of lysogenic bacteria. Most important, perhaps, some of these complexes are very potent anti-tumour agents against a broad spectrum of tumours, and may shortly be used for cancer chemotherapy in humans.

In a truly heroic effort the National Cancer Institute of the U.S. Government has screened approximately 140,000 compounds for anti-cancer activity over the past 15 years. Of this number, however, only a dozen or so were inorganic compounds. This imbalance between organic and inorganic compounds reflects a fashion in chemotherapy that started over 35 years ago. Prior to that, heavy metals were extensively used in medical therapy. About 1935, the discovery of the sulfonamides introduced a new class of organic chemicals which were effective against many bacterial infections. Hard on this came the development of the antibiotics which coupled a high degree of efficiency with a low toxicity. At present, excepting a few outstanding drugs, heavy metals and other inorganic chemicals have ceased to be of active interest as chemotherapeutic agents. The screening program of the National Cancer Institute, occurring within the last 15 years, reflects this bias.

Recently a new class of potent anti-tumour agents has been discovered. These are inorganic complexes of the transition metal Group VIIIb. In this article we shall review briefly the history of this new development and discuss some of the properties that are now known concerning the activities of these compounds. It will be taken as granted that the general reader of this journal will find, as did the author, that biological and medical terminology are "terra incognita". To offset this to some extent, a glossary of the more important terms is appended to the article.

The germinal discovery was made about 1964 when platinum electrodes were used to apply an alternating electric field across a chamber in which bacteria were growing (1). Application of the electric field caused a cessation of all division in the E. coli rods, and since growth was not inhibited, resulted in the appearance of long filaments. A comparison of the normal appearing E. coli rods and the filamentous rods caused by the application of the electric field are shown under the same magnification in Fig. 1. Extensive detective work was required before we could conclude that the effective agent in blocking cell division in the bacteria was a small concentration (~10 ppm) of some platinum complex in solution, electrolytically formed by the applied electric field. It required much further work to determine that these complexes were cis-dichlorodiammineplatinum(II) and cis-tetrachlorodiammineplatinum(IV) (2,3).
The structures of these complexes and some other differently acting agents are shown in Figs 2, 3 and 4. With the verification that these platinum complexes were indeed capable of selectively blocking cell division in bacteria, a series of investigations was undertaken to determine the mechanism and the generality of the effect. VanCamp discovered that the hexachloroplatinum(IV) and tetrachloroplatinum(II) double negative ions are bacteriocides at low concentrations (1 to 6 ppm in the bacterial growth medium). These compounds undergo photochemical changes in the bacterial media, leading to a subsequent replacement of first one and then a second chloride by ammonia. The resulting neutral molecules are not bacteriocides until very high concentrations (~100 ppm in

Fig. 2 Structural formulae of active anti-tumour complexes of platinum. Only a very few specific configurations are active.
solution) are reached. Interestingly, the trans forms of these neutral molecules are not effective in blocking cell division in bacteria, while the cis isomers are. Thus we have two groups of compounds with different bacterial effects; the negative ionic species which are generally bacteriocidal, and the neutral species, in the cis form, which block cell division, but not growth. Gillard and his co-workers have reported similar effects in organic rhodium complexes (4), and Gale, Howe and Smith (5) have extended these observations to include photochemical reactions in ammonium hexachlororidate, which also parallel the platinum transformations and bacterial activities.

A third class of bacterial effects of platinum compounds was discovered much later by Reslova (6). It is known that some strains of E. coli have previously been infected by viruses (bacteriophages) and that the genetic material of the virus was incorporated into and became part of the genetic material of the bacterial cell. The viral genetic material (genome) is repressed in these cells and is not normally detectable. Such bacterial strains are called "lysogenic" for the simple reason that a number of agents, such as ultraviolet light, X-rays, and some chemicals such as the nitrogen mustards (alkylating agents), are capable of inducing the development of partial or complete viruses which lead finally to the destruction (lysis) of the cell. The platinum compounds which are effective anti-tumour agents were found to be extremely potent in inducing lysis of such lysogenic bacteria.

Fig. 5 exhibits the three types of effects on the growth curves in test tubes of various
strains of E. coli reacting to the presence of different compounds of platinum, showing in Fig. 5a the bactericidal effect, in Fig. 5b the cell division inhibition, and in Fig. 5c the lytic effects of these compounds.

Anti-tumour Activity

Since the platinum complexes of Fig. 2 are active in inhibiting cell division in bacteria, it suggested that they may also be interesting compounds to test as anti-tumour agents. Such a study was undertaken in our laboratory. We first determined the level of the platinum compounds which would be tolerated by the animals (LD₅₀ doses), and then whether, below these levels, they would inhibit the growth of transplantable tumours in these animals. The first test was with a
Sarcoma 180 tumour (a standard test tumour in cancer research) in Swiss white mice. We found that the animals would tolerate single injections of cis-dichlorodiammineplatinum(II) at a level (8 mg/kg) which could almost completely inhibit the growth of the transplanted tumour, while the LD₅₀ level was 14 mg/kg. This was the first evidence that these complexes are active anti-tumour agents (7). This compound was then submitted, along with cis-tetrachlorodiammineplatinum(IV) to the National Cancer Institute for screening against the Leukaemia L1210 tumour in mice, their present standard screening tumour. Their results showed that cis-dichlorodiammineplatinum(II) has a potent activity against this tumour, producing an increase in life span of the tumoured animals of 380 per cent, and a "cure" rate of 4 out of 10, with single injections at the therapeutic dose, 8 mg/kg.

In addition to inhibiting the development of newly transplanted Sarcoma 180 tumours in mice, it was later shown that one could wait for a period of 8 days for the transplanted tumour to grow to a very large size, before instituting treatment with the cis-dichlorodiammineplatinum(II). A single injection, intraperitoneally, of 8 mg/kg of this drug caused the complete regression of the large tumours in close to 100 per cent of the animals (8). These results are illustrated in Fig. 6. In addition to producing such extensive "cures" of advanced sarcomas, we found that even up to 11 months afterward, the animals remained immune to a rechallenge with the same tumour. Thus the "cure" produced long-lasting immunity to this tumour system (9).

This first anti-tumour complex of platinum has now been tested extensively on many other transplantable tumour systems. Kociba (10) demonstrated that it can produce 100 per cent "cure" in rats of the Walker 256 carcinosarcoma and the Dunning Ascitic Leukemia. Again, in his studies he has shown that one could wait until the tumour is in a highly advanced state, i.e., four days before the animal would die, before instituting treatment, and still rescue 100 per cent of the animals. The drug has been tested now at the National Cancer Institute and at the Chester Beatty Institute in London by Haddock and Connors (11) on a number of other tumour systems such as the Lewis Lung carcinoma, the B-16 melanocarcinoma, the P388 leukemia, and the ADI-PC6A tumours. It has shown marked effectiveness in all of these tumour systems. The latter group have also shown a lack of activity of the complexes against the Rabbit VX2 carcinoma, the Gardner tumour, and a strain of the Walker 256 carcinosarcoma that is resistant to alkylating agents. At this time, a large number of other laboratories are investigating the anti-tumour activity of these complexes against a host of additional tumour systems. Their results will be reported in the near future. We conclude from this series of studies on the anti-tumour activity of cis-dichlorodiammineplatinum(II) that it is a very effective agent against a wide spectrum of transplantable tumours in animals. Anti-tumour activity has also been exhibited by the other compounds shown in Fig. 2. In some tumour types, other compounds have been shown to be more effective than the cis-dichlorodiammineplatinum(II).

We have then a new class of drugs which could form a set of specific chemotherapeutic agents against specific types of tumours. While transplantable tumours form the best screening systems for evaluating the effectiveness of new anti-tumour agents, there are other types of tumour systems which are more relevant to the cancers that occur in human beings. Two other such types of tumours are those caused by injections of chemical agents (carcinogens) into the animal which induce the formation of tumours, and those which are caused by the injections of certain classes of viruses. It is of interest, therefore, to determine whether these platinum complexes are capable of exhibiting anti-tumour activity against carcinogenically or virally induced tumour systems. Recently, Welsch (12) has investigated the activity of...
The regression of a large Sarcoma 180 tumour in the Swiss white mouse by a single intraperitoneal injection of cis-dichlorodiammineplatinum(II) at the therapeutic dose (8 mg/kg).

cis-dichlorodiammineplatinum(II) against the dimethylbenzanthracene-induced mammary tumour in the rat. He has reported the complete regression of a very large number of extensively developed mammary tumours in the rats, with at least three out of 74 animals completely "cured" of all tumours. Since this particular tumour is the best model system for human mammary tumours, these results are of significant interest. Hinz (13) has tested the same compound against a virally induced tumour of the chicken. The chicks were injected with the Rous Sarcoma Virus, which, after a period of weeks, produces a large Sarcoma tumour in the wing web of the chick. Again, therapeutic doses of the complex were capable of causing complete regression of these tumours in 95 per cent of the animals. From the accumulating results of the anti-tumour activity of some platinum compounds against transplantable, carcinogenically induced, and virally induced tumours we can conclude that these compounds have one of the broadest spectra of action of any class of anti-tumour agents yet discovered. From the fact that it can cause regression of large tumours, and rescue animals when injected a few days prior to their death, we conclude that these compounds are very potent anti-tumour agents.

A major approach of the National Cancer Institute chemotherapy program is the use of combinational drug therapy. The basic idea is to mix drugs, all of which hit the target tumour, but each of which have different side effects. Usually these combination drugs have shown enhanced activity over and above the best of the individual drugs involved. However, only very few
combinations have been found which produced synergism of anti-tumour activity. Recently Venditti (14) showed that a combination of cytoxan (an alkylating agent) and cis-dichlorodiimineplatinum(II) produced a large number of "cures" against advanced leukaemia L1210 in mice, whereas each of them individually produced only a small percentage increase in the lifespan, even up to toxic doses. This would appear to be a very promising method of treatment, since the drugs are both used at levels where side effects are minimal. I will describe below, in the session discussing the mechanism of action of the drug, a possible rationalisation for the apparent therapeutic synergism of these two drugs.

The Toxicological Effects of Platinum Complexes

Experience teaches that it would be overly optimistic to expect an anti-tumour drug to be so specific in its action that it does not at all affect adversely the normal tissues of the body. In general, one finds that all such drugs have side effects which limit the dose levels that can be used in man. It is essential to predict from animal studies the kinds of toxicological effects one may anticipate when the platinum complex is used in human patients. Such studies have been undertaken in a number of laboratories.

It is first necessary to determine how long the drug remains in the animal after a pulse injection, and also its distribution as a function of time in the various organs of the animal. Toth-Allen (15) has evaluated the distribution in mice using a neutron activation technique which is sufficiently sensitive (~0.01 ppm) to measure accurately the low concentration of the platinum complex generally found in tissues (~1 to 5 micrograms per gram of tissue) after injection. She has reported that there is no specific uptake of the platinum complex in the Sarcoma 180 tumour tissue, and that indeed it appears in much higher concentrations in the filtering and excretory organs such as the liver and kidney. However, the damage to these latter organs is negligible, whereas the tumour, of course, is destroyed. A significant fraction (~15 per cent) of the injected drug is still detectable after six days. It has been found, both by Kociba and Toth-Allen, that the drug primarily affects those cells of the body which are most rapidly dividing, such as the cells of the intestinal lining, and of the bone marrow. It is, therefore, a cytotoxic drug, and must be used with caution. These side effects are those generally expected with anti-tumour drugs and techniques for their amelioration have been developed. In the case of the platinum complexes, the damage is always reversible, and the animals recover. They exhibit no long-lasting side effects caused by therapeutic treatment.

The Molecular Biology of Platinum Complexes

The interaction of the platinum complexes with cellular macromolecular syntheses has been investigated by Harder using tissue culture techniques (16). He has measured the ability of treated cells to manufacture nucleic acids (DNA and RNA) and proteins, using radioactively labelled precursors for each of these species. Only those platinum complexes which are active anti-tumour agents are capable of inhibiting the synthesis of DNA. Those which are inactive do not produce such inhibition. Further, at the dose level that appears in the tumour tissues of animals, the DNA replication is selectively inhibited, while RNA and protein synthesis are not inhibited. Similar results have been found by Howle and Gale in vivo (17). Such results are shown in Fig. 7. Harder has further proved that the inhibition of DNA synthesis is not caused by a blockage in the synthesis of the necessary precursors of DNA, nor is the ability of these precursors to enter the cells impaired. We conclude from these data that the platinum complexes most probably act by causing a primary lesion in the DNA of the cell. It is of interest now to determine the nature of this primary lesion.
very effective in inducing lysogenic strains of bacteria. The present understanding of the action of the bifunctional alkylating agents is believed to be the formation of an interstrand crosslink between the guanine bases, at the N-7 position, in double stranded DNA. In order to accomplish this interstrand crosslink, the two active chloride groups must be approximately 8Å apart. In the cis-dichlorodiammineplatinum(II), the spacing between the two active chloride groups is 3.3Å. It would appear, therefore, that such platinum complexes cannot be causing the same primary lesions, i.e., interstrand crosslinking, as do the bifunctional alkylating agents. On the basis of some recent evidence that the platinum complexes inhibit a single stranded bacteriophage as well as it does the double stranded bacteriophage (19); that it reacts in vitro primarily with purine bases rather than pyrimidine bases; and taking into account that the stacking spacing of the bases in the Watson-Crick model of DNA is about 3.4Å, we are led to suggest that the primary lesion caused by the platinum complexes is an intrastrand purine dimer. This is a new type of lesion that has not been investigated before. In vitro studies with purine dimers tend at this time to validate this hypothesis, but much further work must be done to prove or disprove it.

If indeed the platinum complexes do form an intrastrand purine dimer, while the bifunctional alkylating agents form an interstrand crosslink, it may then be that a cellular repair mechanism, which normally operates within the cell to eliminate lesions in the DNA, would have more difficulty in simultaneously repairing both types of lesions, than either one of them individually. This could provide a rationale for the therapeutic synergism described above.

Speculation on the Mode of Action of the Anti-tumour Effects

Reslova (6) has shown that all platinum complexes which are active anti-tumour agents are capable of inducing lysis in lyso-
genic bacteria; those which are non-active do not produce such lysis. These results provide a clue as to the mode of action of the platinum complexes in specifically damaging tumour cells. It has been suggested by a number of scientists that viruses may be the sole agents which transform normal cells into tumour cells. However, since viral particles (virions) are rarely found in tumour tissues, it is more likely that the mechanism of transformation operates after viral infection by the incorporation of the viral genome into the cellular genome. Normally this viral genome is repressed and unable to exhibit its presence. Agents such as X-rays, radiation, other viruses, and chemical carcinogens could partially derepress these viral genomes, forcing the manufacture of a number of new proteins in the cell. It is hypothesised that some of these new proteins are the active agents causing transformation into tumour cells. This hypothesis is consistent with the theory of Hicbner (20). If we now take the evidence of Reslova, obtained from bacterial cells, and apply it to the mammalian cells, we can suggest that the primary lesions in the DNA caused by the platinum complexes act to derepress completely the viral genome. This then leads to the active multiplication of the viral particles, which may or may not be defective. In any case this will almost certainly increase the antigenicity of the cell, and therefore stimulate the immune system to produce retarriatory antibodies to the tumour cells at an enhanced rate. It is also possible that, if the viral genome and the viral particles can be eliminated from the cell without concomitant cell death, the cell should revert back to its normal status. Such effects have been known to occur in the past. This speculation suggests a number of possible tests, and these are under way in a number of laboratories.

Future Outlook

One platinum complex, the cis-dichloro-diammineplatinum(II) is currently on test at the National Cancer Institute in preclinical trials. It is anticipated that it will be tested on human patients some time in the spring of 1971. It will be many months before sufficient clinical data will be available to allow a judgment of the efficacy of this new compound, either alone or in combinational drug therapy, in human tumours.

In the meantime, research must be pursued to develop analogues of the original compounds, and to continue testing these analogues on screening tumour systems. Without hesitation I suggest it is now appropriate for inorganic chemists to join their organic brothers in submitting samples of their syntheses to appropriate Cancer Institutes for screening for anti-tumour activities. In addition to this chemical synthesis activity, it is desirable to know in more detail, and with greater security, the mechanisms of action of this new class of drugs, as well as their general toxicological and pharmacological properties in mammalian systems.

This class of complexes of the platinum group metals form a promising new class of drugs to be added to the medical armamentarium.

References
9. L. VanCamp, 1970, personal communication
12. C. Welch, ibid.
GLOSSARY

Alkylating agent. A reactive chemical which replaces a hydroxyl hydrogen atom by an alkyl group. Bisfunctional alkylating agents have two attachment sites (e.g., nitrogen mustard); monofunctional alkylating agents have one available attachment site (e.g., methylmethanesulphonate).

Antigenicity. Any substance (usually proteinaceous) which when injected into an organism causes the formation of antibodies.

Bacteriocide. Chemical agents which kill bacteria, usually important only if they produce tolerable effects in the host organism.

Bacteriophages. A class of viruses which attack bacteria only.

Carcinogenic. Any agent (chemical, physical, bacterial or viral) which can produce a cancer in an organism.

Carcinoma. A specific form of cancer which is a malignant tumour of lining cells and glands in the body of an organism.

Carcinosarcoma. A mixed tumour with characteristics of both a carcinoma and sarcoma (see below).

Care. A complete disappearance of all detectable symptoms of a cancer for a minimal period of time (in humans, it is usually about five years). The double quote marks usually imply that the results are reported before this minimal time has elapsed.

Cytotoxic. Refers to cell destruction or damage, usually caused by agents detrimental to any essential process of the cell.

Cytokinin. Commercial name for cyclophosphamide, a very potent anti-tumour agent of the bifunctional alkylating agent class.

DNA. Deoxyribonucleic acid. A very long chain polymer consisting of alternating phosphate and sugar groups with attached purine and pyrimidine bases. The genetic information of the cell is coded in the sequence of these bases.

Escherichia Coli (E. coli). A bacterium found in normal intestines. It is probably the most intensively studied organism in biology.

Genome. The total genetic information of a cell.

Interstrand Crosslinks. A chemical (covalent) link between two bases, each situated on one of the two strands of double stranded nucleic acid (DNA, RNA). It is generally believed that this link prevents the separation of the two strands which is necessary for genetic replication.

Intrastrand purine dimer. A chemical bond (covalent) formed between two adjacent purine bases (adenine or guanine) attached to the same strand of a nucleic acid molecule.

In Vitro. Refers generally to experiments done in a cell-free system. Here, however, it also encompasses the growth of mammalian cells in dishes.

In Vivo. Refers to experiments done in an intact organism.

LD₁₀. The dose, given under specified conditions, of any agent, which causes death in 10 per cent of the organisms.

Leukaemia. A mass of relatively undifferentiated cells in uncontrolled growth, disseminated in the blood system. Specifically a disease of the blood and blood forming organs characterized by permanent increase in the number of white blood cells.

Lysis (Lytic). The bursting of a cell caused by the destruction of the cell membrane.

Lysogenic bacteria. Bacteria that contain the genetic information (genome) of a bacteriophage incorporated in the cellular genome.

Melanoma. A tumour containing melanin, the black, polymorphic pigment normally made in special skin cells.

Purines. Aromatic, nitrogen-containing ring molecules (adenine and guanine) with basic properties. One of the two classes of bases defining the genetic code by their sequences in nucleic acids.

Pyrimidines. Cytosine and thymine. The second class of aromatic, nitrogen-containing ring structures, that occur in nucleic acids, and define the genetic code.

Repression (derepression). The forcing of a gene into an inactive state. A repressor molecule, believed to be a protein, blocks substances which turn genes on, or interferes with the genes' ability to eventually produce a specific protein.

RNA. Ribonucleic acid. A long chain polymer consisting of alternating phosphate and sugar groups with attached purine and pyrimidine bases. May be the sole source of genetic information in the organism, and additionally acts as an intermediary to transfer the genetic code into specific protein manufacture.

Rous Sarcoma Virus. An RNA containing virus which is the causative agent of tumours in fowl.

Sarcoma (S-180). A specific form of cancer which is a malignant tumour of supporting tissue in the body of an organism.

Virus (Virion) Defective-Active. Infectious disease-causing agents which are smaller than bacteria and which always require an intact host cell for replication. They may contain either DNA or RNA as the genetic material. The nucleic acids may be double stranded or single stranded. Defective viruses are incapable of infecting host cells, or cannot replicate once their genome has invaded the cell.
Platinum Metals Review is Johnson Matthey’s quarterly journal of research on the science and technology of the platinum group metals and developments in their application in industry

http://www.platinummetalsreview.com/