PLATINUM METALS REVIEW

A Quarterly Survey of Research on the Platinum Metals and
of Developments in their Application in Industry
www.matthey.com and www.platinum.matthey.com

VOL. 48 JANUARY 2004 NO. 1

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Communications should be addressed to: The Editor, Susan V. Ashton, Platinum Metals Review, jmpmr@matthey.com
Johnson Matthey Public Limited Company, Hatton Garden, London EC1N 8EE
Platinum Metals Review: E-Journal

Past editors of this Journal have said, within the confines of the Editorial Department of Platinum Metals Review, that the role of the Journal is to get information from people who didn’t want to part with it and give it to people who didn’t know they needed it.

The information world has changed enormously since those sentiments were first aired. Now, with the intense debate taking place in information circles and academic bodies over publishers fees, authors fees, copyright fees, university publishing and accessibility of scientific papers, it seems to us that this is a good time to extend the services that Platinum Metals Review can offer. In effect it has been decided that as from July 2004, Platinum Metals Review will become purely an E-journal with the editorial team offering a free quarterly E-journal on a dedicated website, with features to enhance the visibility of our authors and be a solid service to our readers.

In line with the original aims of the printed Journal, the E-journal will seek to encourage and stimulate scientific research in the platinum group metals (pgms). It is intended to provide a platform to aid pgm researchers, and provide opportunities and information. The E-journal will continue to be published quarterly as a survey of research on the platinum metals and of developments in their application in industry, as it has for the 48 years of its printed form, to which we will say goodbye with the April issue.

Unlike many online journals and databases, all information on the new Platinum Metals Review website will be accessible. For our authors we will be able to provide a faster, improved publishing service and, unlike at present, we will be less restricted in the number of pages and data we can provide. As many of you know, we spend a lot of time working with our authors, and our enhanced facilities will enable this to be continued and extended.

Having a dedicated website for Platinum Metals Review will enable authors to communicate more widely with other scientists, and indeed with the general public, in ways that the controlled circulation of the printed journal has not allowed, and we hope that you will take advantage of the facilities we will offer.

So, April 2004 will be the last printed issue of this Journal. There will still be some postal communications with our readers and authors after this last issue, but our main contact with you will be electronic, so please send your E-mail addresses to us. We will discuss some of the functionality features of the new website in the April issue.

Speaking on behalf of my colleagues, Pavla White and Keith White, it has been a pleasure to work on the print issues of Platinum Metals Review. We very much appreciate our contacts with authors and readers, and in moving the Journal onwards we look forward to continuing these and to providing a website that will inform, surprise and please you.

Susan V. Ashton
E-mail: jmpmr@matthey.com

The new website for Platinum Metals Review is to be called www.platinummetalsreview.com. You can register now to receive the new Platinum Metals Review E-journal by going to this pre-launch site and filling in your details, or alternately contact the Editor. You will receive an E-mail alert for each new issue, which will link you to summaries, full text versions of new papers and into the site. The ‘Platinum Today’ site: http://www.platinum.matthey.com/publications/pmr-backissues.html will continue to carry links to electronic copies of the Journal.
Improvements to the Microstructure and Physical Properties of Pd-Cu-Ag Alloys

ENHANCEMENT OF THE MECHANICAL AND ELECTRICAL PROPERTIES

By A. Yu. Volkov

Institute of Metal Physics, Ural Branch, Russian Academy of Sciences, 18 S. Kovalevskaya St., 620219 Ekaterinburg, Russian Federation; E-mail: volkov@imp.uran.ru

Ordering and decomposition kinetics of Pd-Cu-Ag alloys having the B2-type superstructure that contain 0 to 30 wt.% silver have been studied. The results of investigations into the microstructure, electrical and mechanical properties are described. Different methods for improving the strength properties of ordered alloys are discussed.

Ordered Cu-(35–50) at.% Pd alloys (B2-type superstructure) have a high corrosion resistance and are distinguished by possessing very low electrical resistivity \( \rho \approx (4–8) \times 10^{-6}\ \text{ohm m} \) (1), two properties which make them of interest to researchers developing functional materials. However, wide-scale use of these alloys is hindered by their relatively poor strength properties: the yield stress of Cu-40 at.% Pd (Cu-40Pd) alloy in the ordered state is only 400 MPa. While, for example, the ordered Cu-Au alloy (L1_0-type superstructure), used as electrical contact material, has a yield stress, \( \sigma_{0.2} = 800 \) MPa.

Studies aimed at improving the functional properties of these Cu-Pd alloys have been undertaken and have resulted in the development of ternary Cu-Pd-Ni alloys with a nearly zero temperature coefficient of electrical resistivity over a wide temperature interval. Alloys Pd-Cu-Au and Pd-Cu-Ag have also been developed and are in use; their yield stresses are in the range 900 to 1100 MPa. However the electrical resistivity of the ternary alloys is higher than that of the initial Cu-Pd binary ordered alloy.

This study will deal with possible methods for strengthening Cu-40Pd alloy and will consider changes in its ordering kinetics and its mechanical and electrical properties after alloying with silver. The results obtained may help towards developing methods to improve the mechanical properties of other ordered alloys.

Materials and Experimental Technique

Various palladium-copper-silver alloys were prepared by vacuum melting palladium (99.98% purity), copper, and silver (99.99% purity), see Table. The alloys were subjected to various

<table>
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<th>Chemical Composition of the Palladium-Copper-Silver Alloys</th>
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mechanical and thermal treatments including annealing at 850°C, quenching in water, and deformation to 75%.

The atomic structure of the alloys was observed by field-ion microscopy (FIM) using wire samples of diameter 0.19 mm. The method of sample preparation and specific features of formation and interpretation of the images in an ion projector have been described in, for example, (2).

A standard heating holder was used when the microstructures of the alloys were being observed in situ in the column of a JEM-200CX transmission electron microscope. The thickness of the foil examined by transmission electron microscopy (TEM) was typically 0.1 mm.

Phase transformation kinetics were analysed from standard four-probe resistometric measurements performed on wire samples of ~ 150 mm long and 0.19 mm in diameter which were placed in an evacuated quartz tube. The device (that is, the quartz tube containing wire samples with four Cu wires as contacts) was placed in a furnace which was either heated to the assigned temperature at a specific rate or preheated, depending on what was required (3).

The strength properties of wire samples 1.5 mm in diameter and 30 mm long were checked by tensile testing.

**Methods for Strengthening Ordered Binary Systems**

Atomic ordering within solid solutions has a huge effect on the physical and strength characteristics of alloys. In some cases atomic ordering is used to produce commercial alloys with a range of optimal properties. However, in-service, plastic deformation may disrupt the long-range atomic ordering, so ways to improve the mechanical properties of ordered alloys are of scientific and practical interest.

Binary alloys, in which planes and directions of dislocation slip become nonequivalent due to ordering (CuAu, CuPt, Ni3Cr, Ni3W, etc.), may acquire high strength properties, thanks to domain-boundary hardening (4). The main factor used for strengthening such alloys is the rearrangement of dislocations as they cross domain boundaries, together with the related consumption of additional energy (5). Thus, refinement of the domain structure causes a big increase in the yield stress of ordered alloys. For example, the yield stress of the CuAu alloy can vary between 115 and 800 MPa depending on its domain structure (6).

A special feature of copper-palladium alloys with $B2$ superstructure is the absence of domain boundaries. Therefore, only the traditional method of strengthening – grain refinement – can be used. After preliminary plastic deformation and subsequent annealing at 300 to 350°C the Cu-40Pd alloy forms an ordered structure with grains ~ 2 µm in size and yield stress $\sigma_{0.2}$ ≈ 500 MPa. The strength properties may be improved a little further if the grains are refined more: by the careful selection of modifying agents.

It has been shown previously that alloys with the $L1_0$ superstructure can acquire an optimal structural state, characterised by high strength and plastic properties (7). This state can be formed by a ‘quick ordering’ of predeformed alloys during annealing over a certain temperature-time interval below $T_c$ ($T_c$ is the critical temperature of ordering). In this case, dislocations inherited from the initial deformed state do not have time to redistribute themselves in the superlattice and so they form a kind of a framework.

The possible ‘inheritance’ of this dislocation framework by $B2$ superstructures has been discussed earlier, taking Fe-Co-Cr as the example (8). It was shown that recrystallisation was retarded when a predeformed alloy was annealed over the temperature interval of fast ordering (9). This treatment may be able to cause strengthening in other ordered alloys with the $B2$ superstructure. In practice the method reduces to short annealings over the temperature interval of the maximum ordering rate. This paper will describe tests of this treatment for enhancing strength properties of Cu-40 at.% Pd alloy.

A kinetic ‘C-curve’ describing the rate of ordering processes in Cu-40Pd alloy was plotted using resistometric measurements on wire samples of the alloy immersed in a salt melt, see Figure 1 (3). The results were used to select temperature-time parameters of annealings for ‘fast ordering alloy’.
Results of mechanical tests on Cu-40Pd alloy pre-deformed to 75% after various treatments are given in Figure 2. Curve 1 corresponds to the initial state of the alloy, that is, after preliminary deformation by drawing to 75%. Curve 4 shows the alloy in the disordered recrystallised state, fixed after annealing at 850°C for 1 hour and subsequent quenching. Curve 3 represents annealing treatment which ends with slowly cooling the samples in the furnace and results in an alloy in a well-ordered recrystallised state. Curve 2 corresponds to a non-recrystallised ordered state. The yield strength of the ordered alloy with non-recrystallised structure (Curve 2) was nearly 250 MPa higher than that of the ordered alloy with recrystallised structure (Curve 3).

From Figure 2 it appears, that we have succeeded in hardening the Cu-40Pd alloy thanks to the dislocation framework inherited from the preliminary plastic deformation. Although the strength properties produced by this method are smaller than analogous values for alloys with L1_0-type superstructure (7), both types of alloys have high plasticity.

While several methods have been proposed and developed for improving the yield stress of ordered alloys, more work needs to be undertaken to find new approaches to hardening.

The Effect of Silver on the Structure and Properties of Cu-Pd Alloy

Above we considered possible methods for hardening ordered binary compounds. Their strength properties can be further improved by alloying. For example, the yield stress of silver-loaded Cu-Au alloy rises to 1000–1400 MPa (from 800 MPa) when a silver-rich phase precipitates on thermal antiphase domain boundaries (10).

Silver alloying of Cu-Pd alloys (B2 superstructure) also improves their strength. In this case, Pd-Cu-Ag alloys are of interest as a functional material for a wide range of applications from stomatology (11) to fabrication of musical instruments (12).

Initial Stages of Ordering and Decomposition in Pd-Cu-Ag Alloys

When alloys of the Pd-Cu-Ag system are annealed at a temperature below the critical ordering temperature, T_o, long-range atomic order is established and the supersaturated solid solution decomposes (13). The ordering kinetics may be estimated most rapidly from an analysis of the temperature behaviour of the electrical resistivity.

Data of the variation of electrical resistivity with temperature for the alloys given in the Table
are shown in Figure 3 (14). These alloys had been deformed to 75% in their initial state. At the beginning of the experiment, electrical resistivity increases a little on heating. However, as temperature continues to increase, ordering within the alloy causes a sharp drop in resistivity. On further heating, the resistivity again increases as the materials become disordered at temperatures above the critical point $T_c$. It appears that electrical resistivity is enhanced and the kinetics of phase transformation are decelerated with an increasing percentage of silver in the alloys.

Structural studies are needed to gain a better understanding of the transformations taking place in the alloys. The initial stages of the processes are of special interest and require analysis by a high-resolution method, such as FIM.

The phase transformation investigated by FIM in the Pd-Cu-Ag alloys (see Table), is one that leads to the formation of a PdCu phase with an ordered b.c.c. lattice and to a silver-rich solid solution (AgPd) with an f.c.c. lattice (11). Our studies of the precipitate microstructure during early stages of the phase transformation, performed using layer-by-layer evaporation of surface atoms, have never shown the formation of just a single phase during the decomposition of a ternary solid solution. On every occasion two phases have precipitated simultaneously and the PdCu phase has always had atomic structure with a high degree of long-range order. The minimum size of particles in both phases was 4–5 nm. As can be seen during evaporation of the atomic layers, the particles had lamellar form.

The progress of ordering and decomposition at later stages may be followed if the alloy foil is heated directly in situ in the column of an electron microscope. For this, a Pd-Cu-Ag alloy containing 20 wt. % silver, ‘Alloy 4’, was used. The boundary between two grains near the edge of the foil was examined, see Figure 4. The test alloy had been initially disordered by quenching after annealing at 950°C for 1 hour. Figure 4(b) shows an electron diffraction pattern for one of the grains in Figure 4(a); it includes satellites near structural reflections (which become more pronounced with the increasing order of the reflection) and splittings in the positions of the superstructural reflections.

The superstructural reflections, divided into pairs in the positions of 100 types and quadruples in the positions of 110 types, have been repeatedly observed in quenched Cu-Pd binary alloys (16), and explained by short-range atomic order. However, it should be emphasised that formation of a structure with short-range order does not lead to the appearance of satellites near structural
Fig. 4 Initial state of the Pd-Cu-20Ag alloy after annealing at 950°C, 1 h, quenching:
(a) microstructure;
(b) diffraction pattern of the upper grain

reflections. Such satellites have been observed in a Pd-25Cu-35Ag alloy (at.%) (17) and appeared as a result of a small difference in lattice constants in the two new phases formed from the matrix. Note that the Pd-25Cu-35Ag alloy did not have an ordered state.

Thus, from the electron diffraction pattern in Figure 4(b) it follows that decomposition was already present in the initial state of the alloy. The alloy contained, on the one hand, microregions enriched with and depleted of the precipitation phase and, on the other hand, groups of copper and palladium atoms having a certain number of neighbours of each species in the nearest coordination spheres.

When the Pd-Cu-20Ag sample (of Figure 4) was heated, the atomic ordering and the decomposition reaction were enhanced. Temperatures and 'holding times' for this alloy are given in Figures 5(a)–5(c). The 'holding times' at certain temperatures were to allow the transmission electron microscope screen image to stabilise and clear, as the image moved and became blurred upon heating the sample. Thermal treatment in the transmission electron microscope column is thus in steps: nearly instantaneous heating to some temperature; a holding period (images and diffraction patterns were taken at the end of the period); heating to the next temperature; another holding period, etc.

The study demonstrated that the silver-enriched
phase could precipitate in the given alloy by two mechanisms: continuous and discontinuous (18). The structure of the interface, which was the preferred nucleation site for new phases, changed little at the first stage. Then, at temperatures up to 400°C discontinuous precipitate plates grew in one of the grains (the lower grain in Figure 5(a)). At temperatures from 400 to 500°C signs of the phase precipitation via the continuous mechanism were enhanced in unreacted regions of the matrix: a parallel Moiré pattern appeared in some regions of the upper grain (Figure 5(b)). The Moiré pattern was due to electron beam diffraction on ensembles of mutually parallel planes having similar interplanar spacings in two superimposed crystals. At temperatures above 500°C (but below \( T_c \approx 600°C \)) continuously precipitated particles grew smoothly and became coarser. They were located in two mutually perpendicular directions of the \(<100>\) type of the initial grain. At elevated temperatures changes also took place in the foil bulk, which decomposed via the discontinuous mechanism. An almost complete grain structure can be seen in Figure 5(b) instead of classical colonies of discontinuous precipitates, which are present in Figure 5(a).

Figure 5(c) presents a two-phase structure, which was formed in the test alloy after heating to 600°C and cooling in the transmission electron microscope column. This structure had grains 0.2–0.3 μm in size. The ability to refine such grains may be a useful method to improve the mechanical properties of Pd-Cu-Ag alloys.

**Changes in the Electrical and Mechanical Properties of Pd-Cu-Ag Alloys during Ordering**

Turning now from the structural evolution of Pd-Cu-Ag alloys to the electrical and mechanical properties, we are especially interested in the Pd-Cu-10Ag alloy, Alloy 2. This is because its electrical resistivity differs least from that of the initial Cu-40Pd binary alloy (see Figure 3).

Figure 6 shows ordering kinetics for Pd-Cu-10Ag, depending on its initial state (heating rate of 600°C h\(^{-1}\)). The initial disordered state was produced either by deformation, by drawing to 75%, (Figure 6(a)) or by quenching after an anneal for 1 hour at 850°C (Figure 6(b)). From the curves it can be seen that the ordering rate in the predeformed alloy is a little larger than in the alloy disordered by quenching from a high temperature. Indeed, the drop in electrical resistivity caused by ordering stopped at 375°C on heating the deformed material. However, the electrical resistivity of the initial quenched alloy was a minimum at 420°C under similar treatment.

It is known that establishment of both the long-range order and the decomposition process affects electrical resistivity. The variation in the kinetic characteristics of phase transformations depending on the initial state of the alloy can be better determined if the electrical conductivity is measured at some annealing temperature. Such experiments were performed with the Pd-Cu-10Ag alloy in one of two initial states: after preliminary plastic deformation or after quenching from a high temperature.

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*Fig. 6 Temperature dependence of the electrical resistivity of the Pd-Cu-10Ag alloy disordered by different methods (heating rate of 600°C h\(^{-1}\)): (a) deformation by drawing to 75%; (b) annealing at 850°C, 1 h, quenching*
between regions of different concentrations. The biggest effect was observed for local regions of different composition, of about 1 nm in size (20). These findings are very similar to our results: namely that as seen by FIM, the size of nuclei in the ageing-phase was about 4–5 nm.

X-ray diffraction (XRD) was used to confirm our findings of the structural and phase transformations in Pd-Cu-10Ag. After preliminary plastic deformation by drawing to 75% the alloy initially had a disordered f.c.c. structure, which was preserved for some time at the initial stage of annealing at 335°C. About 75% of the alloy had an ordered b.c.c. structure after annealing for 35 minutes. The decomposition process was completed when the alloy was kept in the furnace for longer. Thus, the behaviour of electrical resistivity in Figure 7 clearly correlates with structural changes seen in the XRD data of the alloy. Similar results were obtained for the alloy in the initial quenched state.

Figure 8 shows how the electrical resistivity of the alloy depends on the holding times at different temperatures. The shapes of the curves change with increasing temperature; the increase in resistivity immediately before ordering, which is characteristic of low temperatures (see Figure 7), vanishes. The curves in Figure 8 also suggest that the long-range ordering rate was large and that at temperatures above 400°C the ordering process ended before the sample reached the required temperature. This is seen as a rise in resistivity in the curve ‘tails’, connected with increases in electrical resistivity on heating the ordered material, showing a resistivity dependence on growing temperature. For example, from the trend of Curve 2 in Figure 8 it follows that at the furnace temperature of 530°C the ordering processes in Pd-Cu-10Ag were complete 4 minutes after the start of heat treatment (that is, the curve drops to a minimum). However, our measurements showed that the sample had a temperature of ~ 450°C at that moment and heated to the preset temperature in 7 minutes. In this time interval the resistivity increased in the resistometric curves before they flattened out.

The speed of heating the sample in the vacuum

**Fig. 7** The electrical resistivity of Pd-Cu-10Ag alloy vs. the annealing time:
(a) initial state: 75% deformation, annealing temperature 335°C;
(b) initial state: quenching from 850°C, annealing temperature 370°C
tube is low. We placed our device (at room temperature) into the hot furnace and from that moment the temperature of the sample increased and phase transformation started. The phase transformations finished before the sample reached the required temperature. For this reason Curve 2 in Figure 8 again shows an increase in resistivity between 4 and 7 minutes. The plateau for the Curves in Figure 8 appears only after this maximum. Analogous effects connected with a high ordering rate have been detected earlier in Cu-40Pd (6). In order to avoid such effects it is necessary to accelerate the heating of the sample. For example, we used immersion of the sample in the salt melt for drawing the kinetic ‘C-curve’ in Figure 1.

Further experiments were performed to examine transformations in deformed Pd-Cu-10Ag alloy at even higher temperatures. The electrical resistivity again dropped after the start of the experiment, including the case when the alloy was placed in a furnace heated to 850°C. It was not thought earlier that a disordered material placed in a furnace at 250°C higher than $T_c$, had time to become ordered during heating. Moreover, at temperatures just a little higher than $T_c$ the $B2 \rightarrow A1$ transformation rate was small: only partial ordering took place at 630°C after a 3-hour anneal.

The relationship between changes in electrical resistivity during heat treatment and the formation of mechanical properties was also investigated. To this end, the samples underwent mechanical tests in the states when the electrical resistivity curves (Figure 7) included singularities (the minima and maxima on curves $\rho(t)$ and points where $d\rho/d(t) = 0$).

Mechanical and electrical properties usually depend on different structural features of alloys (21). For example, recrystallisation has little effect on electrical resistivity, but causes considerable loss in their strength properties and the growth of plasticity. Ordering will probably not affect mechanical properties, but will lead to a considerable change in electrical resistivity. Figure 3 shows that the electrical resistivity dropped by nearly 3 times. Actually, only small local regions of different concentration may both change the mechanical properties and cause an increase in electrical resistivity.

Figure 9 shows the dependence of: (a) yield stress, $\sigma_{0.2}$, and (b) plasticity, $\delta$, on the annealing time at 335°C for the initial deformed state and at 370°C for the quenched recrystallised state. The mechanical properties of the alloy in the two states changed in completely different ways with annealing time, although their resistivity curves (Figure 7) are similar. When the alloy in the initial deformed state (Curves 1 in Figure 9) was annealed, the yield stress depended little on the heat treatment time: it increased slightly and then dropped at the holding times of 1 and 3 hours (Figure 9(a)). Plasticity increased from 2 to 4% (Figure 9(b)). When the
quenched alloy was annealed for a short time (3 and 7 minutes), the yield stress increased slightly, while plasticity was preserved at a high level (45%). The quenched alloy embrittled sharply (to 0% elongation) on longer heat treatment.

Obviously, the main processes responsible for the deformation behaviour took place during ordering. This is seen by comparing the results of Figure 7 with the mechanical test data in Figure 9. In Figure 9(b), over the time for alloy ordering Curve 1 rises while Curve 2 descends steeply. This again confirmed that the behaviour of the electrical resistivity cannot clearly show the structural changes in the alloy. Indeed, the resistivity curves in Figures 7(a) and 7(b) are similar, but there are different mechanical properties.

Thus, further experiments are needed to improve the plastic properties in the ordered state of the initial deformed Pd-Cu-10Ag alloy. Results of mechanical tests on Pd-Cu-10Ag alloy are given in Figure 10. Curves 1 and 5 show the mechanical properties of the alloy in states: plastic deformation to 75% (Curve 1) and the recrystallised disordered state produced by quenching from 850°C (Curve 5). Curve 4 is given for comparison and shows the variation in mechanical properties when a well-ordered recrystallised state is formed. Curve 2 reproduces one of the results in Figure 6 and describes properties of the initial deformed alloy after annealing at 335°C for 35 minutes.

Curve 3 shows the mechanical properties for alloy annealed at 570°C for 1 hour after a preliminary plastic deformation by drawing to 75%. The alloy became ordered and its plasticity was 12%, which is the highest value among the samples in Figure 10 in which transformation occurred. When this alloy was stretched, the yield stress was followed by a very long plateau and, consequently, Curve 3 has a slightly different trend. All tests of

**Fig. 10 Stress-strain curves for the Pd-Cu-10Ag alloy after different treatments:***
1. 75% deformation (initial deformed state);
2. 335°C, 35 min. quenching;
3. 570°C, 1 h, cooling in furnace;
4. 850°C, 1 h, cooling in furnace;
5. 830°C, 1 h, quenching (initial quenched state)

**Fig. 9(a) The yield stress and (b) plasticity of the Pd-Cu-10Ag alloy:**
1. Initial state: 75% deformation, annealing temperature of 335°C;
2. Initial state: quenching from 850°C, annealing temperature of 370°C
the alloy samples in the initial quenched state were a failure as ordering caused total embrittlement of the material.

Conclusions

Using this data, it is possible to solve the problem of enhancing the strength properties of ordered alloys in the copper-palladium system. One possible variant was discussed at the beginning of this paper; it involves heating the initially quenched Pd-Cu-Ag alloy (containing 20–25 wt.% Ag) to 600°C and subsequent cooling. The two-phase fine-grain structure formed may have a combination of relatively high strength and plastic characteristics.

Another method for strengthening Pd-Cu-Ag alloys containing less than 10 wt.% Ag involves solving the same task considered earlier in (7). Strength properties can be largely improved if an appropriate reinforcing framework is chosen for the plastic matrix. This means the dislocation framework inherited from the preliminary plastic deformation and which is ‘built into’ the ordered matrix. Fine particles of the silver-based phase, formed on the framework dislocations, considerably improve the strength properties of the alloy.

Acknowledgement

This study has been supported by the RFBR (Grant No. 02-03-32159).

References

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The Author

Alexei Yu. Volkov is a Senior Researcher in the Laboratory of Mechanical Properties, Institute of Metal Physics, Ural Branch of RAS, Ekaterinburg. He was awarded his doctorate in 1994. He has worked for nearly 20 years with relationships between microstructure and mechanical properties of ordered alloys based on gold and palladium. His research interests include physical, chemical and mechanical properties of precious metal alloys and their application as functional materials.

Luminescent Osmium(II) Carbonyls

Osmium (Os) atoms are highly effective in promoting spin-orbit interactions due to their heavy molecular weight and could thus make efficient phosphorescent materials.

Researchers from Taiwan have now prepared a new series of octahedral Os(II) carbonyl complexes [Os(CO)X(dbm)] (X = CF3CO2, Cl, Br, I, SCN; dbmH = dibenzoylmethane) by using both solid-state pyrolysis and ligand exchange reactions (Y.-L. Chen, C. Sinha, I.-C. Chen, K.-L. Liu, Y. Chi, J.-K. Yu, P.-T. Chou and T.-H. Lu, Chem. Commun., 2003, (24), 3046–3047). The skeletal arrangement consists of one β-diketonate chromophore (dbm)H to balance the +2 formal charge on the Os, one anionic ligand X and three orthogonal CO ligands located at the octahedral coordination site.

At room temperature, in CH2Cl2, the Os complexes exhibit prominent π→π* phosphorescence, with unusually long lifetimes (29–64 μs) and high quantum yields (0.08–0.13). These complexes have excellent photophysical and electrochemical properties, and may be employed in a variety of photochemical applications, such as organic light emitting diodes or photovoltaic devices.
The London Platinum and Palladium Market

THE ROLE OF THE LPPM IN THE DAILY PRICE FIXINGS OF PLATINUM AND PALLADIUM PRICES

By Tom Kendall
Johnson Matthey PLC, 40–42 Hatton Garden, London EC1N 8EE, U.K.; E-mail: Tom.Kendall@matthey.com

The London Platinum and Palladium Market (LPPM) oversees dealings in platinum and palladium. Twice each day, four members of the LPPM fix the bid prices. The bid price is the price at which LPPM members agree they will buy “good delivery” metal. The bid prices are benchmarks for the market and hence for the industry. Bid prices in turn affect the offer prices that customers are asked to pay for metal. The market values of platinum and palladium, as is the case for all commodities, ultimately affect manufacturing costs. Here, the background to the establishment of the LPPM is summarised and its current role in this important metal market is briefly described.

London has historically been an important centre for the discovery, research in, and development of most of the platinum group metals (1); and also for trading in platinum and palladium. Trade was established in the early 20th century, typically by existing dealers of gold and silver. In 1973 the “London Platinum Quotation” was introduced. This was the forerunner of today’s twice-daily ‘fixings’. The fixings provide a benchmark, at the time, for the price of ‘spot’ platinum and palladium (metal ingot or sheet held in Zurich).

In 1979 the leading London and Zurich dealers decided to standardise the specifications for the quality and origins of the metal they would trade. This metal, originating from accredited smelters and assayers, is termed “good delivery”. In 1987 the informal trading, which had previously taken place between the major (international) companies on a ‘principal-to-principal’ basis, was formalised into the London Platinum and Palladium Market (LPPM), the aim of which is to promote professional trading in London of both platinum and palladium. Currently there are over 35 members of the LPPM (2).

Trading Metal on the LPPM

Platinum and palladium trading takes place during working hours in London and Zurich. The prices for platinum and palladium constantly move in response to worldwide supply and demand, currencies and other economic data, and members of the LPPM compete for business. The metal prices are generally expressed in U.S. dollars per troy ounce, and platinum and palladium are usually traded in multiples of 1000 troy ounces of “good delivery” metal.

The Fixings

In 1989 the London Platinum and Palladium Quotations were upgraded to become full fixings. These fixings, also known as the London Fix, are a snapshot taken twice daily, at 09:45 (am fix) and 14:00 (pm fix) London time, of the varying metal price. At present four members of the LPPM together make the price fixings. These are J. Aron & Co. (U.K.), Engelhard Metals Limited, HSBC U.S.A. London Branch, and Standard Bank London Limited. The fixing process is conducted by telephone, and takes place each day that members are open for dealing in London.

The members of the LPPM fix have an elected Chairman who presides over the fixing. (This Chairman is not the same as the Chairman of the LPPM.) At the start of each fixing, on the basis of prevailing market prices, the Chairman announces an opening price which is relayed to the members’ dealing rooms. This price is relayed to their customers and, on the basis of orders received, members declare as a buyer or a seller.

After members have declared their buying and selling interests, they are asked to state the volumes of metal they wish to trade. If the amounts of
### Requirements for Platinum or Palladium Qualifying as “Good Delivery” for the Market (2)

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<tr>
<td>Form</td>
<td>Plate or ingot</td>
</tr>
<tr>
<td>Weight</td>
<td>Maximum 6 kg (192.904 troy ounces), minimum 1 kg (32.151 troy ounces)</td>
</tr>
<tr>
<td>Purity</td>
<td>At least 99.95% platinum or at least 99.95% palladium</td>
</tr>
<tr>
<td>Markings</td>
<td>Each plate or ingot must bear:</td>
</tr>
<tr>
<td></td>
<td>the producer’s recognised mark;</td>
</tr>
<tr>
<td></td>
<td>the letters PT or PLATINUM with a stamp indicating the purity; similarly for PD or PALLADIUM;</td>
</tr>
<tr>
<td></td>
<td>an individual number or mark;</td>
</tr>
<tr>
<td></td>
<td>the weight in grams or troy ounces (if in grams to one decimal place, if in troy ounces to three decimal places)</td>
</tr>
<tr>
<td>Appearance</td>
<td>Smooth, free from cavities and easy to handle</td>
</tr>
</tbody>
</table>

Buying and selling do not balance, the procedure is repeated, at a higher or lower price, until a balance is achieved. The fixing price is the price at which all the buying and selling orders declared by members are matched.

Customers may be buying or selling metal and can be kept informed of price changes throughout the fixing process. They may alter their instructions at any time until the price is fixed. If all orders cannot be balanced at any price then the fixing price can be determined on the Chairman's discretion. Buyers of metal may choose to buy in the market, or to buy at the time of the fixing. In the latter case they will not know in advance what the fix price will be. (The price has been known to move considerably between fixes!)

Sellers of “good delivery” metal at the fix will receive the fixing price; buyers pay a small premium. Settlement (exchange of money and metal) takes place two working days after the fixing date.

The fixing prices act as a reference point for the platinum industry, and are widely published. The fix is a bid price for 'loco Zurich plate', that is, the price that the LPPM fixing members are prepared to pay for spot platinum or spot palladium, at that fix time.

The market-making members of the LPPM act as principals, issue their own contracts, and quote buying and selling prices of platinum and palladium metal. Other parties may also quote prices.

**“Good Delivery”**

This describes the standards to which platinum or palladium must conform to be acceptable to the LPPM. To facilitate trading the LPPM maintains a list of melters and assayers: “The London/Zurich Good Delivery List”. The standards for platinum and palladium are in the Table (2).

**Conclusions**

Although the prices of platinum and palladium are continuously changing in response to many different external influences, the fixing prices are a valuable reference point within the spot market. In effect, the fixing price represents matched orders from customers across the world to buy or sell. The fixings make it transparent to interested parties: supplier, consumer, dealer or investor, the price at which all current dealings have been satisfied.

**References**

2. www.lppm.org.uk

**The Author**

Tom Kendall is Publications Manager at Johnson Matthey, Hatton Garden, London. His main interests are the supply and demand of the platinum group metals.
METAL PRICES AND THE COST OF PGM CHEMICALS

The selling price of chemicals that contain the platinum group metals (pgms) is made up of two major aspects: manufacturing costs and the metal price. For metal compounds made from the most used (and more costly) pgms: platinum, palladium and rhodium, the manufacturing element of the total cost is relatively small, typically around 0.5 to 1.5%. Therefore, for large-scale use of manufactured metal compounds involving platinum, palladium and rhodium (1), the overall cost is directly related to the intrinsic metal value in the compound. This cost is, however, often offset as these metals can be recycled, and this reduces the impact of the market price on the overall economics of the process.

However, for the less commonly used (and less expensive) pgms: iridium, ruthenium and osmium, the manufacturing element of producing metal compounds can range from 20 to 70% of the total cost. The price of such compounds is still influenced by movements in the intrinsic metal price, but to a lesser extent.

The human, technological and investment efforts required of the primary producers (the mining companies) to extract and refine the ore cannot be overstated (2). While the market, responding to supply and demand, functions for the well-being of the pgm industry as a whole.

John E. Gourd

References
1 www.jmcatalysts.com/pct/
2 www.platinum.matthey.com/production/africa.html

The Author
John Gourd is the Commercial Manager of Precious Metal Products at Johnson Matthey, Royston. His main professional responsibilities are the supply of precious metal salts and compounds.
E-mail: John.Gourd@matthey.com

Palladium Perovskite Catalysts for Suzuki Couplings

Palladium (Pd)-containing perovskites have the ability to self-regenerate under oxidative and reductive conditions, while suppressing growth of metallic Pd particles, so could be useful in automotive emissions control (1). These properties could also promote activity and long life in catalysts used in organic synthesis, where similar problems in catalyst deactivation occur.

Now researchers from the University of Cambridge, U.K., have studied Pd perovskites, such as LaFeO$_3$:CoO$_{3}$:Pd$_{0.05}$O$_3$, as catalysts for cross-coupling reactions, during Suzuki reactions of aryl halides and boronic acids (2). It was found that aryl bromides cross-coupled with boronic acids in the presence of 0.05 mol% Pd catalyst with K$_2$CO$_3$ as base to give the requisite biaryls in high yields (95%). Aqueous alcohols were identified as effective solvents and heating to 80°C. The catalyst was removable from the reaction mixture.

In order to study the scope and limitations of the catalyst, a reaction using 1 g of 4-methoxybromobenzene and 1 mg of (0.0038 mol% Pd) catalyst was performed. This resulted in a 93% conversion corresponding to a turnover number of 27,000.

ICP-MS showed particularly low levels of residual Pd which suggests that the catalyst may operate by a ‘release and capture’ mechanism, with the perovskite acting as a reservoir and scavenger for the active catalytic species. This perovskite functioned as an air-stable, reusable catalyst for Suzuki cross-coupling under mild conditions, with low levels of Pd leaching.

References

Replicating Magnetic Nanostructures

A single-step, non-contact, large-area, high resolution process for effective patterning of a complete magnetic recording structure has been reported by a team from Germany and Austria (A. Dietzel, R. Berger, H. Loseschner, E. Platzgummer, G. Stengl, W. H. Bruenger and F. Letzkus, Adv. Mater., 2003, 15, (14), 1152–1155).

Using large area Ar+ ion projection, direct structuring was achieved via a stencil mask a significant distance from the surface of a 1”-format hard disk. This transferred a complete magnetic nanostructural recording pattern to a Co/Pt multilayer.
Platinum Group Metal Chalcogenides
THEIR SYNTHESES AND APPLICATIONS IN CATALYSIS AND MATERIALS SCIENCE

By Sandip Dey and Vimal K. Jain
Novel Materials and Structural Chemistry Division, Bhabha Atomic Research Centre, Mumbai 400085, India
*E-mail: jainvk@apsara.barc.ernet.in

Some salient features of platinum group metal compounds with sulfur, selenium or tellurium, known as chalcogenides, primarily focusing on binary compounds, are described here. Their structural patterns are rationalised in terms of common structural systems. Some applications of these compounds in catalysis and materials science are described, and emerging trends in designing molecular precursors for the syntheses of these materials are highlighted.

Chalcogenides are a range of compounds that primarily contain oxygen, sulfur, selenium, tellurium or polonium and which may also occur in nature. The compounds may be in binary, ternary or quaternary form. Platinum group metal chalcogenides have attracted considerable attention in recent years due to their relevance in catalysis and materials science. Extensive application of palladium (~ 27% of global production in year 2000) in the electronic industry in multilayer ceramic capacitors (MLCCs) and ohmic contacts has further accelerated research activity on platinum group metal chalcogenide materials.

The platinum group metals form several chalcogenides:

- binary,
- pseudo-binary for example, Ru1-xOxS2, Ni2Ru1-xS2, etc., and
- ternary, such as spinels: M'M2E4 (M' = Cr, Mn, Fe, Co, Ni, Cu; M = Rh, Ir; E = S, Se, Te) and Tl2Pt4E6 (E = S, Se, Te); MoRuS, etc. These differ in stoichiometry and structures. Several of the chalcogenides occur in nature as minerals, for instance, laurite (RuS2), braggite (PdPt2S6), luberoite (Pt6Se16), PdAgTe8, etc. Although there is an extensive literature on the synthesis and structural aspects of bulk platinum group metal chalcogenides, only recently has there been research into their catalytic and electronic properties, and into the preparation of nanoparticles and thin films.

This review intends to cover these emerging aspects of platinum group metal chalcogenides and will consider first a selection of the structures adopted, followed by their catalytic and electronic uses.

**Ruthenium and Osmium Chalcogenides**

Ruthenium and osmium dichalcogenides of composition ME2 (M = Ru, Os; E = S, Se, Te) are usually prepared by heating stoichiometric quantities of the elements in evacuated sealed ampoules at elevated temperatures (~ 700°C) (1–3). Single crystals, such as RuS2, see Figure 1, are grown either from a tellurium flux (4) or by chemical vapour transport techniques using interhalogens as transporting agent (5). This latter technique,

![Figure 1: Structure of RuS2 (pyrite structure) (77). The black circles are Ru and the open circles are S](image)

Table I

Crystallographic Information and Band Gap of Ruthenium/Osmium Chalcogenides

<table>
<thead>
<tr>
<th>MₓEᵧ</th>
<th>Crystal system</th>
<th>Space group</th>
<th>Cell parameter, Å</th>
<th>JCPDS-ICDD #</th>
<th>Band gap, eV*</th>
<th>Shortest M-E and E-E bond lengths, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>RuS₂</td>
<td>cubic</td>
<td>Pn₃</td>
<td>5.610</td>
<td>80-0669</td>
<td>1.22 (opt.) (19)</td>
<td>2.3520(3)(13) 2.4707(2)(13) 2.1707(8)</td>
</tr>
<tr>
<td>RuSe₂</td>
<td>cubic</td>
<td>Pn₃</td>
<td>5.933</td>
<td>80-0670</td>
<td>0.76 (opt.) (19) ≥ 0.6 (el.) (14)</td>
<td>2.4707(2)(13) 2.4532(2)</td>
</tr>
<tr>
<td>RuTe₂</td>
<td>cubic</td>
<td>Pn₃</td>
<td>6.391</td>
<td>79-0252</td>
<td>0.39 ± 0.01 (opt.) (24) 0.25 (el.) (14)</td>
<td>2.647(8) 2.791</td>
</tr>
<tr>
<td>OsS₂</td>
<td>cubic</td>
<td>Pn₃</td>
<td>5.619</td>
<td>84-2332</td>
<td>~ 2.0 (opt.) (14)</td>
<td>2.352(8) 2.210</td>
</tr>
<tr>
<td>OsSe₂</td>
<td>cubic</td>
<td>Pn₃</td>
<td>5.946</td>
<td>73-1693</td>
<td>&gt; 0.2 (el.) (14)</td>
<td>2.647(8) 2.826</td>
</tr>
<tr>
<td>OsTe₂</td>
<td>cubic</td>
<td>Pn₃</td>
<td>6.397</td>
<td>84-2333</td>
<td>26</td>
<td></td>
</tr>
</tbody>
</table>

* Band gap measured from optical (opt.) or electrical resistivity (el.)

employing Cl₂/AlCl₃ as the transport agent, has been exploited, for example, to prepare a low temperature modification of α-RuTe₂, which crystallises in the marcasite structure. The orthorhombic space group is Pnmm (No. 58) (a = 5.2812(13), b = 6.3943(19), c = 4.0085(13) Å) (6). This low-temperature (marcasite) phase transforms into the pyrite structure at 620°C (7).

Extensive structural studies both by powder (8–12) and single crystal (13, 14) X-ray measurements on ME₂ show that these compounds adopt a pyrite (FeS₂) structure, and crystallise in a cubic system with space group Pa₃, see Table I. The chalcogenide ions in these structures are tetrahedrally surrounded by another anion (E⁻) and three metal ions. The metal ions occupy the tetrahedral holes formed by the anion sublattice, see Figure 1.

Magnetic susceptibility measurements on ME₂ indicate diamagnetic behaviour (15). Infrared and Raman spectra of pyrite-type ME₂ have been reported (16–19). A comparison of the Raman and IR frequencies shows that the corresponding metal-chalcogen and chalcogen-chalcogen bonds have nearly the same strengths (at least for RuS₂ and RuSe₂) (17), but the metal-chalcogen bond strength increases in the order: Ru < Os (18). Of the five expected absorptions for ME₃, the MTe₂ compounds display only one phonon peak in the Raman spectra which indicates the metallic behaviour of the tellurides (19). Studies of their optical absorption (15, 20–22), electrical resistivity (15, 20, 23–25) and Hall effect measurements (23–26) have shown that ME₂ are indirect band n-type semiconductors.

Rhodium and Iridium Chalcogenides

Rhodium and iridium form a variety of chalcogenides differing in stoichiometry and structural patterns, see Table II. At least four different families of compounds can essentially be identified:
- ME₂ (Rh₅S₅, Rh₅Se₅, Rh₅Te₅, Ir₅S₅, Ir₅Se₅, Ir₅Te₅)
- M₂E₃ (Rh₂S₃, Rh₂Se₃, Ir₂S₃)
- Rh₃E₄ (E = S, Se, Te) and
- M₁E₈ (Rh₃Se₈, Rh₃Te₈, Ir₃Te₈).

Additionally, other rhodium chalcogenide stoichiometries have been isolated and these include Rh₃S₇, Rh₃Se₇, Rh₃Te₇, and Rh₃Te₈.

Rhodium and iridium chalcogenides are usually prepared by sintering (at 650–1100°C) pressed stoichiometric mixtures of the constituent elements in evacuated sealed ampoules (27–35). Single crystals, for example, Rh₅S₅, are prepared by chemical transport techniques (for example, using bromine as a transport agent) (29) and tellurium flux techniques (for example, for Ir₅Te₅) (36).

Rhodium and iridium chalcogenides are usually
diamagnetic, with a few exceptions, such as Rh$_3$S$_4$, which shows temperature-independent paramagnetism (35). The compounds display metallic to semiconducting behaviour (28, 33, 35–40).

The structures of these compounds have been established by powder as well as by single crystal X-ray diffraction methods. The compounds show diverse structural preferences, such as pyrite-type, Cd$_2$I$_3$-type or NiAs structures. For instance, MTe compounds (M = Rh or Ir) exist in a NiAs structure while ME$_2$ compounds adopt pyrite- and

Table II
Crystallographic Information and Band Gaps of Rhodium/Iridium Chalcogenides

<table>
<thead>
<tr>
<th>$M_xE_y$</th>
<th>Crystal system</th>
<th>Space group</th>
<th>Cell parameters</th>
<th>JCPDS-ICDD #</th>
<th>Band gap, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$a, \text{Å}$</td>
<td>$b, \text{Å}$</td>
<td>$c, \text{Å}$</td>
</tr>
<tr>
<td>RhS$_2$</td>
<td>cubic</td>
<td>$\text{Pna} \bar{3}$ (205)</td>
<td>5.58</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Rh$_2$S$_3$</td>
<td>orthorhombic</td>
<td>$\text{Pbn} \bar{m}$ (60)</td>
<td>8.462</td>
<td>5.985</td>
<td>6.138</td>
</tr>
<tr>
<td>Rh$_3$S$_5$</td>
<td>cubic</td>
<td>$\text{Pm} \bar{3} \text{m}$ (221)</td>
<td>9.911</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Rh$_3$Se$_5$</td>
<td>cubic</td>
<td>$\text{Cm} \bar{m}$ (21)</td>
<td>10.29(2)</td>
<td>10.67(1)</td>
<td>6.212(8)</td>
</tr>
<tr>
<td>Rh$_2$Se$_6$</td>
<td>hexagonal</td>
<td>$P$</td>
<td>7.296</td>
<td>–</td>
<td>10.986</td>
</tr>
<tr>
<td>Rh$_2$Se$_8$</td>
<td>orthorhombic</td>
<td>$\text{Pbn} \bar{m}$ (60)</td>
<td>8.888</td>
<td>6.294</td>
<td>6.423</td>
</tr>
<tr>
<td>Rh$_3$Se$_8$</td>
<td>cubic</td>
<td>$\text{Pna} \bar{3}$ (205)</td>
<td>6.009</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Rh$_2$Se$_2$</td>
<td>rhombohedral</td>
<td>$\text{R} \bar{3}$ (148)</td>
<td>8.490</td>
<td>–</td>
<td>10.196</td>
</tr>
<tr>
<td>Rh$_3$Te$_2$</td>
<td>hexagonal</td>
<td>$\text{P6} \bar{3} \text{mmc}$ (194)</td>
<td>3.990</td>
<td>–</td>
<td>5.660</td>
</tr>
<tr>
<td>Rh$_2$Te$_3$</td>
<td>cubic</td>
<td>$\text{Pna} \bar{3}$ (205)</td>
<td>6.441</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Rh$_3$Te$_4$</td>
<td>orthorhombic</td>
<td>$\text{I}2 \text{m}$ (12)</td>
<td>6.812</td>
<td>3.954</td>
<td>11.23</td>
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<tr>
<td>Rh$_3$Te$_8$</td>
<td>rhombohedral</td>
<td>$\text{R} \bar{3}$ (148)</td>
<td>6.425</td>
<td>–</td>
<td>90.724</td>
</tr>
<tr>
<td>IrS$_2$</td>
<td>orthorhombic</td>
<td>$\text{Pnam}$ (62)</td>
<td>19.79</td>
<td>5.624</td>
<td>3.567</td>
</tr>
<tr>
<td>Ir$_2$S$_3$</td>
<td>orthorhombic</td>
<td>$\text{Pbcn}$ (60)</td>
<td>8.487</td>
<td>6.019</td>
<td>6.169</td>
</tr>
<tr>
<td>IrSe$_2$</td>
<td>orthorhombic</td>
<td>$\text{Pnam}$ (62)</td>
<td>20.95</td>
<td>5.938</td>
<td>3.742</td>
</tr>
<tr>
<td>IrTe$_2$</td>
<td>hexagonal</td>
<td>$\text{P} \bar{3} \text{m}$ (156)</td>
<td>3.930</td>
<td>–</td>
<td>5.386</td>
</tr>
<tr>
<td>Ir$_3$Te$_8$</td>
<td>cubic</td>
<td>$\text{Pna} \bar{3}$ (205)</td>
<td>6.414</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

Fig. 2 Structures of IrTe$_2$ (Cd$_2$I$_3$ system) (above) and RhTe$_2$ (pyrite system) (right) (41)
CdI₂-type structures, see Figure 2 (28, 31, 32, 34, 40–42). Although RhS₂ has been reported, it seems that the pure compound does not exist as attempts to prepare it have resulted in the formation of Rh₅S₈, RhS₃ and other phases (28). RhTe₂ adopts the pyrite structure, see Figure 2, but does not exist as a stoichiometric compound above 550°C (41).

IrTe₂

IrTe₂ shows polymorphism with three phases:
- 3D polymeric 2D-derived CdI₂-type (h-IrTe₂ because of its hexagonal cell)
- pyrite-type (c-IrTe₂ because it is cubic), and
- monoclinic (m-IrTe₂) (28, 41).

These three phases and four hypothetical phases (ramsdellite-type, pyrolusite-type, IrS₂-type and marcasite-type) have been analysed by extended Hückel tight-binding electronic band structure calculations (34, 43). Monoclinic IrTe₂ (m-IrTe₂) shows structural features of both CdI₂ and pyrite-type IrTe₂ (c-IrTe₂) phases (34). The high pressure behaviour of h-IrTe₂ was studied at up to 32 GPa at room temperature and two new forms were obtained (44). The first structural transition took place at ~ 5 GPa and led to the monoclinic form (m-IrTe₂). The second transition occurred at 20 GPa and gave rise to the cubic pyrite phase (c-IrTe₂) (44).

IrSe₂

The structure of IrSe₂ is similar to the marcasite system (42), as are the structures of IrS₂ and the low-temperature modification of RhSe₂ (a = 20.91 (3), b = 5.951(6), c = 3.709(4) Å) (28). Each iridium atom of IrSe₂ is located at the centre of a distorted octahedron with three Se neighbours at a distance of 2.44 Å and three others at 2.52 Å. Half of the Se atoms are tetrahedrally surrounded by three iridium atoms and one selenium atom, the Se-Se distance being 2.57 Å. The other half of the Se atoms have a similar neighbourhood, but adjacent Se atoms are spaced at 3.27 Å (42).

M₂E₃

The structures of M₂E₃ (Rh₂S₆, Rh₂Se₆, Ir₂S₆) are isomorphous (29) and the metal atoms adopt an octahedral configuration. Every octahedron shares a common face with another octahedron to form octahedron pairs. These pairs are arranged in layers of stacking sequence ABABA... Four metal atoms surround each chalcogen atom at the vertices of a distorted tetrahedron.

M₃E₈

The compounds M₃E₈ (Rh₃Se₈, Rh₃Te₈, Ir₃Te₈) exist in a pyrite-type structure (41, 45–47) and crystallise with rhombohedral symmetry. The structure is a three-dimensional network made of interlinked E₂ pairs, see Figure 3.

Rh₃E₄

Rh₃E₄ (E = S, Te) adopts the NiAs structure and crystallises in a monoclinic system (35). The structure of Rh₅S₈ consists of edge sharing Rh₅S₆ octahedrons which are connected by S₂ pairs (S-S = 2.20 Å). The molecule contains Rh₆ cluster rings in a chair conformation with the Rh-Rh single bond length of 2.70 Å. Both fragments are linked by common S atoms (35). Structures of Rh₁₁S₁₅ (48) and Rh₁₂Te₈ (49) have also been established by single crystal X-ray structural analysis.

Palladium and Platinum Chalcogenides

Palladium and platinum form a wide variety of chalcogenides. They are prepared by heating the required amounts of two elements in an evacuated sealed tube. The material thus obtained is made
<table>
<thead>
<tr>
<th>MₓEᵧ</th>
<th>Crystal system</th>
<th>Space group</th>
<th>Cell parameters</th>
<th>JCPDS-ICDD #</th>
<th>Band gap, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>a, Å</td>
<td>b, Å</td>
<td>c, Å</td>
</tr>
<tr>
<td>PdS</td>
<td>tetragonal</td>
<td>P42/m (84)</td>
<td>6.429</td>
<td>–</td>
<td>6.611</td>
</tr>
<tr>
<td>PdS₂</td>
<td>orthorhombic</td>
<td>Pbcn (61)</td>
<td>5.460</td>
<td>5.541</td>
<td>7.531</td>
</tr>
<tr>
<td>Pd₁₆S₇</td>
<td>cubic</td>
<td>I4/m (217)</td>
<td>8.930</td>
<td>–</td>
<td>–</td>
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<tr>
<td>Pd₂₄S</td>
<td>cubic</td>
<td>P</td>
<td>8.69</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Pd₄S</td>
<td>orthorhombic</td>
<td>Ama2 (40)</td>
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<td>5.374</td>
<td>7.453</td>
</tr>
<tr>
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<td>tetragonal</td>
<td>P42₁c</td>
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<td>–</td>
<td>5.590</td>
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<tr>
<td>PdSe</td>
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<td>P42/m (84)</td>
<td>6.711</td>
<td>–</td>
<td>6.395</td>
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<tr>
<td>Pd₁₇Se₁₅</td>
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<td>Pm3m (221)</td>
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<td>–</td>
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<tr>
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<td>P2₁₂₁₂ (18)</td>
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<td>6.873</td>
<td>10.172</td>
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<tr>
<td>Pd₃Se</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Pd₇Se</td>
<td>orthorhombic</td>
<td>P2₁₂₁₂ (18)</td>
<td>5.381</td>
<td>6.873</td>
<td>10.172</td>
</tr>
<tr>
<td>Pd₇Se</td>
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<td>–</td>
<td>–</td>
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<td>5.394</td>
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into powder and annealed at various temperatures (50), often for several days (as in the synthesis of PtS and PtSe) (51, 52). The palladium-sulfur (53), palladium-selenium (50), palladium-tellurium (54), platinum-selenium (55) and platinum-tellurium (56, 57) systems have been investigated by differential thermal analysis and X-ray powder diffraction methods.

In the palladium-tellurium system at least eight binary phases (PdTe, PdTe₂, Pd₃Te₂, Pd₄Te₅, Pd₆Te₁₅, Pd₇Te₇, Pd₈Te₉, and Pd₁₀Te₃) have been identified and characterised by X-ray diffraction (54). The platinum-tellurium system on the other hand exhibits only four binary phases (PtTe, Pt₃Te₂, Pt₅Te₃, and Pt₇Te₇) (57, 58). These compositions are constant and there is no appreciable compositional range. The Pt₅Te₇ is stable up to ~675°C whereas Pt₇Te₇ melts above 1000°C. The band structures of some of these chalcogenides (PtS (58), PtSe (59, 60), PtSe₂ (60)) have been determined by first principle electronic structure calculations. Semiconducting behaviour for some of these compounds has been noted (58, 60–62).

The binary palladium and platinum chalcogenides show a higher diversity of structures than found for the Rh/Ir and Ru/Os compounds. Besides several other binary phases, see Table III, four general families have been isolated:

- ME (PdS, PdSe, PdTe, PtS, PtSe, PtTe)
- PdₓEₚ (E = S, Se, Te)
- PdₓEₚ (E = S, Se, Te), and
- MEₕ (PdS₂, PdSe₂, PdTe₂, PtS₂, PtSe₂, PtTe₂).

Single crystal X-ray analysis of PdSe shows that there are three crystallographically unique Pd atoms, each site being in a slightly distorted square-planar environment. Each of the two crystallographically independent Se atoms is coordinated by a distorted tetrahedron of Pd atoms (63).

PdTe crystallises in the NiAs structure and can be modelled as a single h.c.p. lattice.

PdS₂ and PdSe₂ exist in a deformed pyrite-type structure (50), while the remaining ME₅ adopt a CdI₂ structure. PdTe₂ has a layered structure with the layers stacking along the (001) direction, see Figure 4. The Pd⁺⁴ cations are octahedrally coordinated. The layers are formed by octahedra sharing edges along the [010], [010] and [110] directions. The Pd-Te bond distance is 2.693(2) Å (64).

Although the single crystal X-ray structure of Pd₁₅Se₁₅ can be analysed in any of the three space groups, viz. Pm₃m, P4₃m and P432, refinement based on the first space group gives the lowest standard errors (65). There are four crystallographically different palladium atoms, see Figure 5. One of the palladium atoms has a regular octahedron of selenium atoms with Pd-Se distances of...

---

*Fig. 4 Structure of PdTe₂ (64)*

*Fig. 5 Structure of Pd₁₅Se₁₅ (65)*
2.58 Å. The remaining three palladium atoms are coordinated each with four selenium atoms either in a flattened tetrahedron (one Pd centre) with average Pd-Se distances of 2.48 Å or square plane (two Pd atoms) with Pd-Se distances of 2.53 and 2.44 Å. The square planar palladium atoms are also coordinated to palladium atoms with Pd...Pd distance of 2.78 Å.

**The Use of Platinum Group Metal Chalcogenides in Catalysis Hydrodesulfurisation**

Several platinum group metal sulfides, particularly RuS₂, have been extensively employed as catalysts for hydrodesulfurisation (HDS) reactions (66–79). It has been shown that semiconducting transition metal sulfides, such as PdS, PtS, Rh₂S₅, Ir₂S₅, RuS₂, have higher catalytic activity than the metallic sulfides (66). They have been used, supported on γ-Al₂O₃ or carbon, or as bulk catalysts, for HDS of several thiophene derivatives, such as thiophene, 3-methylthiophene, benzothiophene, dibenzothiophene or 4,6-dimethyl dibenzothiophene, see Equation (1).

\[
\text{R} \quad \text{catalyst} \quad \text{S} \quad (1)
\]

In RuS₂ the three coordinate surface Ru atoms, such as those found on the (111) surface, appear to provide active sites for HDS (77). The temperature programmed desorption profiles indicate that two different adsorbed species that have different relative concentrations are a factor for the degree of reduction caused by RuS₂. NMR results suggest that one of the species leads to the formation of SH groups while the other species has hydridic character (80). To study the effect of the surface Ru-S coordination number on the surface S-H and Ru-H species for thiophene adsorption on RuS₂, a topology study of the Laplacian of electron density of selected (100) and (111) surfaces was carried out (81, 82). Acidic Lewis and Brensted sites are created in mild reducing conditions. The Lewis acidic sites play an important role in activating sulfur-containing molecules and subsequently in their transformations. Hydrogenation properties are related to Ru sites with a low S coordination (83).

Thiophene adsorption on stoichiometric and reduced (100) surfaces of RuS₂ has been studied using ab initio density functional molecular dynamics. On the stoichiometric RuS₂ surface, thiophene is adsorbed in a tilted η¹ position where the sulfur atom of the thiophene molecule forms a bond with the surface Ru atom similar to that in bulk RuS₂; but there is no activation of the molecule. The formation of sulfur vacancies on the surface creates a chemically active surface and the possibility for thiophene adsorption in the η² position when the thiophene molecule is activated (84, 85). Scattered-wave calculations on model catalyst clusters and catalyst-thiophene (or related compounds) systems have indicated that ππ bonding between the S atoms of the catalyst and the S and C atoms of thiophene is responsible for binding the thiophene molecule to the catalyst in the initial stages of the HDS process (86). Electronic and bonding properties of the RuS₂ and related thiophene adsorption systems have also been studied by discrete vibrational-Xe calculations (87).

The cleavage of the sp² carbon-heteroatom bond in the hydroprocessing of substituted benzenes, such as aniline, phenol, diphenylsulfide, chlorobenzene, over unsupported transition metal sulfides at 250°C and 70 bar H₂ pressure was studied. Hydrogenolysis of the sp² carbon-substituent bond results from attack by a soft nucleophile, such as an hydride ion, on the carbon bearing the substituent (88).

**Hydrodenitrogenation**

The activity of a carbon-supported metal sulfide catalyst in the hydrodenitrogenation (HDN) of quinoline increases in the order: Ni < Pd < Pt (89). Platinum group metal chalcogenides have been employed in HDN reactions (89–93) and the activity is related to the acidic-basic properties of the active phase. The best catalyst appeared to have a good balance between the acidic-basic properties responsible for C-N and C-C bond cleavage and labile superficial S anions, which, in a reducing atmosphere, leads to a large number of active sites for hydrogenation reactions (93). Ruthenium and rhodium sulfides gave only a low
conversion of quinoline to hydrocarbons (propylbenzene and propylcyclohexane) (89), while the hydrodenitrogenation of quinoline, decahydroquinoline, cyclohexylamine and o-propylamine over Rh and Ir sulfide catalysts was shown to lead to the formation of hydrocarbons (90, 94).

Hydrotreatment of naphtha, which contains mainly nitrogen (pyridines, anilines and quinolines), sulfur- and oxygen-containing heteroatom compounds (92), has been carried out on transition metal sulfides which were used for the removal of nitrogen compounds.

**Hydrogenation Reactions**

Platinum group metal chalcogenides have also found use as catalysts in hydrogenation reactions (95–102). Sulfides (PdS₅, Ir₂S₃, OsS₂ (95)), selenides (Ru₂Se₃ (96)) and tellurides of Rh, Pd and Pt have been used for the reduction of nitrobenzene to aniline in 95–99% yield. The catalysts are insensitive to sulfur poisoning and are active at low temperatures and low hydrogen pressure. The reductive alkylation of aniline and substituted anilines on Ru, Rh, Pd or Pt selenides/tellurides has also been carried out (96). For instance, aniline was converted to isopropylaniline in the presence of ruthenium selenide (Ru₂Se₃) catalyst, see Equation (ii) (96):

\[
\text{PhNH}_2 + \text{CH}_3\text{COCH}_3 + \text{H}_2 \xrightarrow{\text{Ru}_2\text{Se}_3, 180^\circ \text{C}} \text{PhNHPPh} \tag{ii}
\]

Palladium sulfide catalysts are active for the hydrogenation of thiophenes (thiophene, 2-methylthiophene and benzothiophene) to tetrahydrothiophenes, Equation (iii), (97–101).

\[
\begin{align*}
\text{S} \quad & \xrightarrow{2\text{H}_2/\text{catalyst}} \quad \text{S} \\
\text{2H}_2/\text{catalyst} \quad & \xleftarrow{2\text{H}_2/\text{catalyst}} \\
\end{align*}
\tag{iii}
\]

In these reactions hydrogenation and hydrogenolysis often proceed simultaneously. Thus, the hydrogenation of thiophene yields thiolute and the hydrogenolysis products, butane and H₂S, which are formed during the decomposition of thiophene and thiolute (97). PdS supported on aluminosilicate showed higher activity (by 1 to 2 orders of magnitude) than Rh, Ru, Mo, W, Re, Co and Ni sulfides (101).

Pyridine hydrogenation to piperidine has been investigated using ruthenium sulfide supported on Y-zeolite or alumina catalysts (103).

RuS₂ supported on a dealuminated KY-zeolite showed very high activity (roughly 300 times that of an industrial NiMo/Al₂O₃ hydrotreating catalyst) for the hydrogenation of naphthalene to tetralin (104).

Both palladium sulfides and platinum sulfides have been employed for hydrogenation reactions, such as the hydrogenation of a gasoline pyrolysis residue over Pd sulfide/Al₂O₃ (105), and the hydrogenation of naphthalene to tetralin over carbon-supported Pd or Pt sulfide (78).

The hydrogenation of diethyl disulfide gives ethanethiol with selectivity > 94% at atmospheric pressure in the presence of supported transition metal sulfide catalysts (102). Bimetallic catalysts were less active than monometallic compounds in this reaction. Both bulk and SiO₂ supported palladium sulfides have been employed for the production of methanol from the hydrogenation of CO (106, 107).

**Isomerisation and Acetoxylation Reactions**

Solid bed catalysts containing Pd/Se or Pd/Te on a SiO₂ carrier have been employed for the isomerisation of alkenes, particularly 3-butene-1-ol (108). Besides isomerisation, Pd/Te or Pt/Te supported on SiO₂ have been used to prepare unsaturated glycol diester compounds by treating a conjugated diene (such as butadiene) with a carboxylic acid (such as acetic acid) in the presence of oxygen (109). This process, see Equation (iv), has been industrialised by Mitsubishi Kasai Corp. for the production of 1,4-butanediol from 1,4-butadiene (110). The production of unsaturated glycol diesters (such as 1,4-diacetoxy-2-butene and butanediols) comprises reacting a conjugated diene with the carboxylic acid and O₂ in the presence of a solid Rh-Te catalyst (111). A Rh₆Te catalyst (~ 3%) on activated charcoal has been used for the acetoxylation in AcOH of 1,3-cyclopentadiene to diacetoxy-cyclopentane (112).
Dehydrogenation Reactions

Platinum group metal chalcogenides have found use in dehydrogenation reactions. The dehydrogenation of tetrahydrothiophene over RuS₂ yields thiophene in 92% yield (Equation (iii)) (113). The active sites for the hydrogenation and hydrodesulfurisation are anionic vacancies in the sulfide catalysts (RuS₂). The higher lability of S₂⁻ anions relative to S⁻² anions in a reducing atmosphere explains the higher activity of RuS₂ (93). The catalytic dehydrogenative polycondensation of 1,2,3,4-tetrahydroquinoline using transition metal sulfides (PdS, PtS, RuS, RhS₃) provides a direct route to the synthesis of unsubstituted quinoline oligomers. RuS gives a maximum yield of 97% (114, 115).

The photocatalytic decomposition of H₂O into H₂ and O₂ takes place over RuS₂ powder as well as over RuS₂ supported on various substrates (such as SiO₂, zeolites) under UV irradiation (116–118).

Platinum Group Metal Chalcogenides as Semiconductors and in the Electronics Industry

Platinum group metals (particularly Pd and Pt) are used for low resistance ohmic contacts in semiconducting electronic devices. For device reliability thermodynamically stable contacts are very important. Therefore reactions occurring at the interface between the metal contacts and the II-VI semiconductors have been extensively studied in recent years (119–133). For instance, it has been found that at the interface of Pt/CdTe diffusion couples a nonplanar reaction layer of the intermetallics CdPt and PtTe is formed (121).

The crystallographic microstructure and electrical characteristics of platinum group metals (mainly Pd) and Ni or Au ohmic contacts on ZnSe and on p-type (001) ZnTe layers have been investigated as a function of annealing temperature. The specific contact resistance of these contacts depends strongly on annealing temperature and the palladium layer thickness (122).

In Pd/ZnSe, palladium forms a ternary epitaxial phase PdₓZn1₋ₓSe at 200°C which is stable up to 450°C while platinum begins to form Pt₃Se₄ at 575°C at the Pt/ZnSe interface (119).

PdS and PtS have been employed as light image receiving materials with silver halides (134, 135). Photographic film containing 6–10 mol m⁻² PdS coating gives dense black images with high contrast (136). In optical disc recording films PdTe₂ is one of the active components (137). Palladium sulfide has also been used for lithographic films (138, 139) and lithographic plates with high resolution (140, 141). Semiconducting films of metal sulfide polymer composites were obtained when organosols of PdS in DMF were prepared from Pd(OAc)₂ and H₂S, and followed by addition of polymers (142).

Thin films of PdS and PtS have been deposited on GaAs substrate from [M[S₂CNMe(c-Hex)]₃] (M = Pd or Pt) by low pressure MOCVD (143). The complexes also serve as precursors for the growth of nanocrystals of PdS and PtS which are formed by thermolysis of the complex in tri- octylphosphine oxide (143).

PdS thin films have been deposited onto Si and quartz substrates at 10⁻² torr from a single source precursor [Pd(S₂COPr)₃]. Two different vapour deposition processes: photochemical (308 nm laser irradiation) and thermal (350°C) were employed (144). The PdS films are in the polycrystalline tetragonal phase. Palladium sulfide in a polymer matrix has been used for the manufacture of semiconductors and solar cells (145). Semiconducting
and photoelectrochemical properties of PdS have also been investigated (146).

PtS₂ nanoclusters synthesised from PtCl₄ and (NH₃)₂S in inverse micelles show an indirect band gap of 1.58 eV as compared to 0.87 eV for bulk PtS₂. Nanoclusters with double the mass show a band gap of 1.27 eV (147).

Aqueous dispersions of PdS particles have been prepared from PdCl₂ or Na₂PdCl₄ with Na₂S solutions. Uniform spherical particles of diameter 20–30 nm were obtained in acidic medium in the presence or absence of surfactants. Surfactants of the AVANEL S series enhanced deposition of PdS particles on an epoxy circuit board (148).

Thin films (0.05–1 μm thick) of pyrite-type RuS₂ (polycrystalline or epitaxial) have been grown on various substrates such as silica, sapphire and GaAs, by MOCVD using ruthenocene and H₂S as precursors (149). The films have been characterised by X-ray diffraction, microprobe and SIMS analysis, and electrical and optical measurements.

The BARC group has recently designed several molecular precursors for the synthesis of palladium chalcogenides (150–154). The compound [Pd(Spy)(S₂P(OPr)₂)₂(PPPh₃)] containing a chelating dithiophosphate group (Figure 6) undergoes a three-stage decomposition leading to the formation of PdS₂ at 357°C (150). The dimeric methylallyl palladium complexes, [Pd₂(μ-ER)₂(η³-C₄H₇)₂] afford polycrystalline Pd₄E (E = S or Se), see Scheme, and amorphous Pd₃Te₂, the former at moderately low temperatures (refluxing xylene)

![Scheme](image)
and the latter at room temperature (151). Thermogravimetric analysis of \([\text{PdCl}(\text{SeCH}_2\text{CH}_3\text{NMe}_2)_3]\), and \([\text{PdCl}(\text{SeCH}_2\text{CH}_3\text{NMe}_2)(\text{PR}_3)_2]\) (PR$_3$ = PPh$_3$ or Ptol$_3$) reveals that these compounds undergo a two-step decomposition leading to polycrystalline Pd$_2$Se$_{15}$ (153). The thermogravimetric analysis of \([\text{PdCl}(\text{Te(3-MeC}_3\text{H}_2\text{N}))_2](\text{PPh}_3)]\), see Figure 7, shows that the compound decomposes in a single step at 290°C to give PdTe (by XRD, Figure 8) as aggregates of microcrystals (by SEM, Figure 9) (154).

**Conclusions**

The great structural diversity and catalytic applications (HDS, HDN, hydrogenation, etc.) of platinum group metal chalcogenides, seem to offer new avenues for further research. Clear trends seem to be emerging in molecular precursor chemistry for the preparation of metal chalcogenides. It is believed that such trends would provide opportunities to isolate not only known stable or metastable phases at low temperatures (for instance palladium allyl complexes (151)) but also as yet unknown stoichiometries. It is hoped that this brief review will serve as an interface between scientists working in areas such as mineralogy, catalysis, materials science and solid state structural chemistry.

**Acknowledgements**

We thank Drs J. P. Mittal and S. K. Kulkshreshtha for encouragement of this work. Also, many thanks for permission to reproduce some of the Figures in this article.

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The Authors

Sandip Dey is a Scientific Officer in Novel Materials and Structural Chemistry at Bhabha Atomic Research Centre (BARC), Mumbai, India. He has an MSc (1996) from Burdwan University and was selected for the “Advanced Course on Chemical Sciences and Nuclear Sciences” of BARC. He has a PhD (2003) from Mumbai University (Jain). His interests are the chemistry of platinum chalcogenolates and NMR spectroscopy.

Vimal K. Jain is Head, Synthesis and Pure Materials Section, Novel Materials and Structural Chemistry at BARC. He has an MSc (1976) from Agra University and PhD (1981) from Rajasthan University, and was a Post Doctoral Fellow at the University of Guelph, Canada. In 1984 he was appointed as Scientific Officer in the Chemistry Division, BARC. His research interests include inorganic and organometallic chemistry of the platinum group metals and main group elements, design and development of molecular precursors for advanced inorganic materials, and multinuclear NMR spectroscopy.

Imprinting Polymer with Palladium

A palladium ion imprinted polymer (Pd IIP) with nanopores, capable of preconcentrative separation of Pd, has been synthesised by a team from CSIR, India (S. Daniel, J. M. Gladis and T. Prasad Rao, *Anal. Chim. Acta*, 2003, 488, (2), 173–182). The Pd IIP was synthesised by the thermal copolymerisation of Pd(II)–dimethylglyoxime–4-vinylpyridine ternary complex, styrene and divinylbenzene in the presence of 2,2’-azobisisobutyronitrile as initiator. IIP particles were obtained using cyclohexanol as the porogen, followed by leaching with 50% HCl to remove the Pd.

In tests, the IIP could extract Pd ions from dilute aqueous solutions. The IIP particles had much higher selectivity towards Pd over Pt and base metals found in noble metal deposits, and 100 times higher distribution ratio than an ion recognition (blank) polymer. Also, γ-irradiation was found to enhance the extraction of Pd particles into leached IIP particles compared to unirradiated ones.
Palladium in Restorative Dentistry

SUPERIOR PHYSICAL PROPERTIES MAKE PALLADIUM AN IDEAL DENTAL METAL

By Roy Rushforth
Charles Booth Ltd, 49–63 Spencer Street, Birmingham B18 6DE; E-mail: royrushforth@bettsmetals.co.uk

For the last century or so the first stage of treating a decayed tooth has involved ‘drill and fill’ procedures: the decay within a tooth is cleaned out by drilling and the tooth ‘restored’ by filling the clean cavity with a mercury based amalgam or more recently with a non-metallic filler. However after several such treatments the tooth can no longer be repaired by this technique and more radical restorative procedures are necessary. The dentist must now prepare a clean tooth stub that can be capped or crowned with a tailor-made metal crown manufactured by a dental technician using specialised processes. A bridge is formed when two or more adjacent teeth are to be restored by this means. The alloys used to produce these restorations are crown and bridge alloys.

Since the late 1970s, palladium has been a key metal used worldwide by the dental industry in the development of alloys for the manufacture of crown and bridge restorations constructed by dental technicians. The price of palladium, now significantly less than that of either gold or platinum, coupled with its much lower specific gravity, (12.02 compared to 19.3 or 21.45 g cm\(^{-3}\), respectively) ensures that palladium-based alloys are very economic (the same weight of palladium has a larger volume than gold or platinum).

Palladium also has a good range of solubility with several metals (helpful for alloying) and an ability to impart good mechanical properties. It has excellent tarnish/corrosion resistance and biocompatibility in the oral environment. These properties make it ideally suited for use in dental crown and bridge alloys (those fitted in the as-polished state), see Figure 1. Generally such palladium-based alloys are ‘white’. However, many gold-based alloys also contain small amounts of palladium (typically 1–5 %) to improve resistance to tarnishing and corrosion without significant loss of colour (1).

These properties are also important for the

---

Fig. 1  A four-unit bridge in metal of two molar and two premolar teeth in the left-hand side lower jaw. The dental technician built up the mould using lost wax casting from impressions of the jaw made by the dentist. As our jaw structures are unique, each bridge or crown has to be individually made

Fig. 2  A four-unit bridge for the right hand side of an upper jaw. The bridge is of 2 molars and 2 premolars. The teeth have been mostly made in ceramic with some metal being permitted to be seen in the less noticeable rear molar. The dental porcelain and the dental alloy will be heat and expansion-compatible
Properties of a Typical Palladium and a Typical Gold Dental Alloy

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<th>0.2% Proof stress, MPa</th>
<th>Thermal expansion, K⁻¹</th>
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</tbody>
</table>

The development of lightweight palladium alloys intended for coating with porcelain, where the final restoration has to match the surrounding (natural) teeth (2). Such alloys, called porcelain, bonding or ceramic alloys, need to be compatible with the dental porcelains in terms of high temperature stability and coefficients of expansion.

The high melting point of palladium is an essential property contributing to this form of restorative dentistry, as the high firing temperatures of most porcelains (950–1020 ºC) require that the alloy has a higher melting point so it does not melt or collapse. This temperature clearly needs to be higher than those of the alloys (palladium or otherwise) used for conventional crowns and bridges. Even more important is the low thermal coefficient of expansion of palladium. This value is lower than that of most other metals including silver, gold and platinum, and is helpful when developing lightweight porcelain alloys compatible with currently-used dental porcelains that are fired in several layers onto the prepared metal crown, see Figure 2.

The porcelain alloys must typically possess thermal expansivities of 13.7 to 14.9 K⁻¹ over the range 0–500 ºC if ‘blowing off’ or cracking of the porcelain during the cooling cycle of layer build-up is to be avoided. Properties of a typical palladium and comparable gold-based dental alloy are shown in the Table. Many gold porcelain alloys also benefit from the attributes that palladium additions impart and as such can contain between 7–40% Pd.

Together with the current advantageous price of palladium (~ U.S.$198/troy oz in December 2003) (3) compared to gold (~$409/troy oz), the valuable combination of intrinsic mechanical and physical properties that palladium possesses make it unique among the precious metals. Only its anomalous price (4) between Spring 2000 and mid-2001, peaking at ~ $1094/troy oz in January 2001 before falling to its current level, has impacted on the use of palladium-based alloys. Less-favoured non-precious metal alloys, based on nickel, chromium and cobalt-chromium, gained ground during this period. However with the current stability in prices, the continuing use of palladium in precious metal restorations seems assured.

There is yet another type of palladium alloy compatible with lower temperature fusing porcelains with expansions in the range 15.8–16.9 K⁻¹ and which is fired at ~ 800 to 850 ºC. These alloys can be used for either ordinary crown and bridge restorations or be subsequently coated in the lower temperature porcelains. These are more popular in the U.S. and Europe but not yet in the U.K.

References

Standards
BS EN ISO 9693:2000 Metal-ceramic dental restorative systems
BS EN ISO 8891:2000 Dental casting alloys with noble metal content of at least 25% but less than 75%
BS EN ISO 1562:1995 Dental casting gold alloys

The Author
Roy Rushforth is Managing Director of Charles Booth (Stephen Betts Group) a U.K. dental alloy manufacturer supplying precious and non-precious materials for crown and bridge restorations. His 38 years’ experience in platinum group metals and gold has been first at Johnson Matthey where he developed new alloys and processes for the jewellery and dental businesses, then at the Birmingham Assay Office, U.K., as Development Director.
The Eighth Grove Fuel Cell Symposium
DEVELOPING A FUEL CELL MANUFACTURING INDUSTRY

By Donald S. Cameron
The Interact Consultancy, 11 Tredegar Road, Reading RG4 8QE, U.K.; E-mail: DCameronInteract@aol.com

The Eighth Grove Fuel Cell Symposium was held at the ExCeL Exhibition Centre in London Docklands from the 24–26th September 2003, with the theme “Building Fuel Cell Industries”. Fuel cells have already been widely demonstrated as highly efficient, reliable and durable power generators with emissions characteristics superior to any conventional technology. The main barrier to their being generally adopted is the need to reduce their initial cost, and the means to achieve this formed the underlying theme of the Symposium.

As an indication of the growing importance of fuel cells, the Symposium was sponsored by seventeen organisations, including the U.K. Department of Trade and Industry (1), the European Fuel Cell Group, and the U.S. Fuel Cell Council, in addition to a host of commercial organisations. The Symposium, organised by Elsevier Advanced Technology, attracted almost 600 delegates. Thousands more attended the accompanying exhibition, where the 110 stands gave an indication of the rapid growth of the industry. Static exhibits as well as mobile vehicles were on display and visitors were invited to ride some of the fuel cell powered scooters and cycles. In total, this constituted the largest display of fuel cell technology ever seen in Europe.

The Symposium was formally opened by Jenny Jones, the Deputy Mayor of the Greater London Authority, who highlighted the three hydrogen powered fuel cell buses which will become operational in London this year. These form part of the 30-bus Clean Urban Transport for Europe (CUTE) programme, complementing the efforts by the London Hydrogen Partnership to promote the use of renewable energy.

Jenny Jones also presented the Grove Medal to Professor Ferdinand Panik of DaimlerChrysler AG for his pioneering work in developing fuel cell road vehicles. Professor Panik suggested that fuel cell powered buses may be commercially viable within the next ten years, partly due to the feasibility of refuelling them from a central point. More general implementation for passenger vehicles will require a hydrogen refuelling infrastructure to be set up. The commercial viability of small passenger vehicles will also be dependent on the cost of fuel cells approaching the $45 kW⁻¹ target proposed by the U.S. Department of Transport. Professor Panik expected them to begin to become commercially viable by about 2012, with Toyota, Honda and DaimlerChrysler already demonstrating their small fleets (around 60 vehicles in total) in North America, Europe, Japan and Singapore. A number of collaborative efforts such as the California Fuel Cell Partnership, and the European bus project will help to gain acceptance of the technology.

The Symposium was divided into ten sessions, some being held in parallel, and covered all types of fuel cells, hydrogen provision, demonstrations of technology, and associated topics, such as financing and possible government incentives. It began with talks by representatives from a number of major industries on their company’s experience of entering the fuel cell market. These included component suppliers, fuel cell manufacturers, an electric utility and an energy supplier. However, this review is limited to developments involving the uses of the platinum group metals (pgms).

The Exhibition
The exhibition was a major feature of the Symposium, with a wide variety of organisations emphasising the range of technologies needed to manufacture and market fuel cells, and a growing number of specialist material and component suppliers. The static devices on display included: a HotModule 300 kW molten carbonate fuel cell (MCFC) built by MTU CFC Solutions (2), Ballard AirGen PEMFC (proton exchange membrane fuel
An Airgen portable generator built by Ballard Power Systems in Canada, based on a 1.2 kW PEM fuel cell. Its applications include uninterruptible power supply (UPS) for computers and on-site power generation. Its retail price is ~ U.S. $6000. The generator is presently fuelled by compressed hydrogen, however, hydrogen stored in metal hydride canisters is expected to be available soon.

cell) portable generators, a TCP solar powered traffic light system, Heliocentris Energiesysteme educational fuel cells, and many others.

An area large enough to drive full size passenger vehicles was set aside for regular demonstrations of fuel cell powered vehicles. The fuel cell powered vehicles on display included a DaimlerChrysler F-Cell (the fuel cell powered version of the Mercedes A-class), two examples of the Ford Focus powered by fuel cells, and vehicles built by the Scottish Fuel Cell Consortium, RE-fuel, and others. Significantly, there were also a number of small two wheeled scooters and motor assisted bicycles, several of which were available to be ridden by members of the public.

**Market Issues**

David Jollie (Fuel Cell Today) emphasised the need for cost reduction in the fuel cell industry, comparing the cost of power in internal combustion engines for cars at U.S.$ 100 kW⁻¹ with the current cost of fuel cells at $4000 kW⁻¹ to $10,000 kW⁻¹. However, there are a considerable number of less cost-sensitive applications, such as portable computers, mining locomotives, buses and military generators. In terms of fuel cell technologies, transport will be dominated by low temperature PEMFCs, while small portable and micro devices are likely to be methanol or hydrogen fuelled PEMFC types. Small stationary and residential fuel cells of 1–10 kW will probably be dominated by

*A Ford Focus FCV at the Fuel Cells Canada stand. A similar vehicle was driven from the Canadian Embassy in central London to the exhibition in very heavy traffic, to give regular demonstrations.*

- Peak power: 67 kW (90 hp)
- Peak torque: 190 Nm (140 ft-lb)
- Peak efficiency: 91%

The fuel cell is a PEM of the Ballard Mark 900 Series.*
PEMFCs or solid oxide fuel cells (SOFCs), while local power stations larger than about 250 kW are likely to be solid oxide or molten carbonate electrolyte types. It is likely that success in reducing the cost of PEMFCs for motor vehicles will also lead to a higher proportion of PEMFCs being used for other applications. The number of fuel cells built to date is increasing rapidly, with some 3500 at the end of 2002 and 6500 anticipated by the end of 2003, and there are now 20,000 people employed in the fuel cell industry.

Platinum Availability

It has sometimes been suggested that the full exploitation of low temperature fuel cells may be limited by the availability of the pgms. Mike Steel (Johnson Matthey) posed the question of how much platinum is likely to be required, and whether the increased demand can be met. Bill Ford of the Ford Motor Company, has forecast that by 2025, one quarter of all light vehicles will be powered by hydrogen.

Assuming that each car will require about 75 kW of fuel cell power, and using the U.S. Department of Energy target of 0.2 g kW⁻¹ of platinum, Mike Steel estimated that platinum demand for fuel cell cars could be 150–300 tonnes per year by 2025. This compares with a production rate of 180 tonnes per year in 2000, and proven reserves of 5000 tonnes, with inferred reserves of 30,000 tonnes of platinum, but does not include platinum recovered and recycled, a practice already developed for automotive emissions control catalysts in the advanced economies of the world. Mike Steel reached the conclusion that platinum is a key catalyst for PEMFC development, and that there should be sufficient resources available to meet the needs for the foreseeable future.

Fuel Cell Users

Andreas Willeke (E.ON Energie) presented an interesting perspective from a fuel cell user. The E.ON Group was formed by the union of the German VIAG and VEBA groups, which then incorporated Ruhrgas in Germany, and PowerGen in the U.K. With annual sales exceeding €37 billion, E.ON is purely a technology user company, interested in evaluating fuel cells for industrial and residential use. They are willing to evaluate pre-commercial fuel cells in practical field tests, and offer suitable facilities.

Currently E.ON have 5 of 250 kW units in operation or planned using a range of fuel cell technologies. For residential fuel cells, E.ON is working with affiliated companies on two publicly funded projects with 9 systems in operation. Their largest project, which is internally funded, involves a field test of up to 200 systems in the homes of customers. However, few systems in a suitable ‘pre-commercial production’ stage are available from fuel cell manufacturers. To date, 6 units have been installed, and this number is expected to rise to over 100 units in the next 3 years. Should these prove successful, E.ON plans to purchase fuel cells and operate them at the premises of...
customers, and sell the power and heat. This may help to overcome the capital cost and credibility barriers which invariably beset new technologies.

**Materials and Components for PEMFCs**

Low temperature PEMFCs, which utilise pgm catalysts, are being developed for a wide variety of applications. A number of papers emphasised efforts being taken to reduce the cost of individual components, particularly the polymer membranes and separator plates which incorporate gas flow channels. At the same time, the intrinsic costs of catalysts are being reduced by their more effective utilisation and by increasing the power density of the fuel cells.

Simon Cleghorn (W. L. Gore & Associates) described improvements made to their membrane electrode assemblies (MEAs) since the 1990s. Validation tests on their PRIMEA® Series 56 MEA for stationary fuel cells suggest that lifetimes in excess of 20,000 hours are achievable. Operating at 70°C and 75% relative humidity of fuel and dry air at 25 psig pressure and 2 × stoichiometric flow rate, typical voltage decay rates are 4–6 μV/hour at 800 mA cm⁻² current density, compared to an ultimate target of 1 μV/hour for a 40,000 hour lifetime.

The PRIMEA® Series 57 MEA is intended for automotive systems, using less than 1 g kW⁻¹ of platinum, and operating at less than 50% relative humidity at 80°C and 270 kPa pressure, with high power density and 1500 hours durability in frequent start/stop duty cycles. The PRIMEA® Series 58 MEA, currently under development, is intended for hydrogen fuelled portable power applications, with no external reactant humidification and using forced air cooling.

Accelerated voltage decay rate tests are also being used to assess membrane characteristics. Fluoride ion release rates provide an indication of the degradation of the membrane. Typically, a membrane can lose up to 25% of its total fluoride ion concentration before failure occurs. The latest life test data suggest that technologies are available which may be capable of meeting the 40,000 hour life target in stationary applications (this is generally accepted as an adequate length of time for stationary applications). Advanced electrode development is also being carried out for cell operation at over 95°C, with new membranes capable of operating at up to 120°C.

Improved membranes can contribute to the success of the PEMFC, and Dennis Curtin (DuPont Fuel Cells) outlined work being carried out on Naftion® perfluorosulfonic acid (PFSA) polymer separator materials, which are some of the ones most widely used in the industry. Membrane conductivity is a function of its water content, and membranes are typically used at temperatures lower than 90°C, with relative humidity greater than 80%. The formation of peroxide species is largely responsible for degradation of the membranes, with attack by the peroxide radical on polymer end groups having residual H-containing terminal bonds generally believed to be the principal mechanism. The peroxo radical attack is most aggressive at low relative humidity (30% RH) and temperatures exceeding 90°C. Chemical modifications are being used to reduce the number of end groups and thereby stabilise the polymer.

Solvent-based and water-based processes are used to convert the polymeric materials into dispersions used to formulate inks and catalyst coatings, while membrane films are prepared by solution casting to prepare continuous rolls for subsequent processing into MEAs.

Steven Grot (Ion Power Inc.) detailed their efforts to manufacture lower cost MEAs for fuel cells and electrolysers using DuPont Naftion®. This is achieved first by reducing the thickness of the solution-cast membranes to only 25 μm, and second, by replacing the expensive ion-exchange membrane material around the peripheral sealing area of the cell by DuPont Kapton® polyimide film.

Separator plates also constitute a major cost component of fuel cells, and Falko Mahlendorf (ZBT, University of Duisberg-Essen) described their efforts to produce low cost bipolar plates using injection moulding techniques. Thermoplastic materials, mixed with high loadings of carbon to provide electrical conductivity, are prepared and then injection moulded into flat plates. The filled
polymer conductivity is directly proportional to the amount of carbon incorporated, over a wide range of compositions, although typical loadings of 50% carbon provide rather less conductivity than pure graphite. However, experience with small (50 cm² area) 20-cell fuel cell stacks indicates that the lower intrinsic conductivity of injection moulded plates is partially offset by the better homogeneity and production tolerances of the injection moulded product. Separator plates of 140 mm × 140 mm × 4 mm are projected to cost as little as €0.6 each, depending on the numbers required.

Micro Fuel Cells

The functions of many items of electronic equipment are limited by the power supplies available. To improve on existing primary and secondary storage batteries, several electronic manufacturers are working on small direct methanol oxidation fuel cells, and also combinations of miniature reformers and PEMFCs.

Stefan Wagner (Fraunhofer Institute for Reliability and Microintegration, Germany) described the construction of miniature PEMFCs of 1 mm² to 1 cm² intended to be used as battery replacements. In long term tests on pure hydrogen, the 0.54 cm² cells operated at 100 mA cm⁻² with a voltage of 400 mV, using naturally convected air at room temperature.

Robert W. Reeve (QinetiQ, U.K.) described the cylindrical fuel cells they have developed which can operate on a range of fuels, although the use of alkaline electrolyte, combined with the direct oxidation of methanol or sodium borohydride is preferred. The cylindrical structure allows a weight ratio of stored fuel to cell hardware of 1:1, with an active electrode area of 10 cm². Individual cells can be joined at their ends to provide useful output voltages.

Yet another option is to operate micro scale PEMFCs using hydrogen supplied from miniature reformers running on hydrocarbons. Jamie D. Holladay (Battelle Pacific Northwest Division, U.S.A.) described the construction of steam reformers running on methanol, natural gas, diesel or jet fuel (JP-8). Initially, Battelle is developing a steam reformer for a hybrid system with 25–100 W electric power operating on reformed methanol. The 25 W system, with a reformer volume under 20 cm³ and mass of less than 150 g is postulated to have a total 14-day mission weight of 8 kg compared to 38 kg for primary batteries or 57 kg for secondary batteries. This equates to an energy density of 1500 Wh kg⁻¹. Even higher energy densities (1732 and 1600–2150 Wh kg⁻¹) should be achievable for 50 and 100 W systems, respectively.

Demonstrations of Fuel Cells

Mike Binder (U.S. Army Engineer Research and Development Center (ERDC)), provided an update on the trials of their 30-strong fleet of fuel cells which have been in progress for 10 years in regions ranging from the Alaska to the Mojave Desert. These 200 kW phosphoric acid type fuel cells supplied by ONSI have provided high reliability and availability for over 825,000 operating hours, and verified the manufacturer’s claims for low pollution characteristics. ERDC also manages the Department of Defense Climate Change Fuel Cell Program, which provides a rebate of $1000 kW⁻¹ to applicants who purchase a U.S.-manufactured fuel cell. So far this has helped to fund 18.8 MW of phosphoric acid fuel cells, 170 kW of PEMFCs, 1.0 MW of MCFCs and 505 kW of SOFCs. Emphasis is currently on 1–20 kW residential fuel cells for installation at U.S. military or related facilities. The devices must be turnkey installations, needing no more than annual maintenance, and providing over 90% availability for use. To-date, 21 residential-type fuel cells have been operated under the 2001 programme with over 93% availability. The best of these, 5 kW units supplied by Plug Power achieved 98.8% availability over the last 11.5 months of the trial. A further 32 units are being purchased under the 2002 budget and others are planned from the 2003 appropriations. It is hoped to install one such device in the U.S. Embassy in London.

Andre Martin (Ballard Power Systems AG, Germany) mentioned that over 1000 of their Nexa™ 1200 W power units have been sold. These have achieved certification by Underwriters Laboratories (UL) in the U.S.A. and Canadian Standards Association (CSA) and can operate on
reformate gas as well as pure hydrogen. They are being incorporated by the original equipment manufacturers (OEMs) into uninterruptible power supplies, standby generators and small electric vehicles. Several examples of these were displayed in the exhibition.

Considerable progress has been made by MTU CFC Solutions and Fuel Cell Energy Inc. in developing MCFC generators. These were presented by Michael Gnann. Following the first field trial in Germany, 9 of these large combined heat and power installations are operating in Europe and the U.S.A. Locations include hospitals, a shipyard, an electric utility, and a car factory, and further units are being delivered to North America and Japan. Overall energy recovery from these plants varies between 70% and 90% depending on the installation. The 300 kW HotModules are being adapted to run on secondary gases such as biogas, sewerage and synthesis gas, and are being scaled up to 1 MW modules for multi-MW generators. Although these high temperature fuel cells are not dependent on pgms for their operation, they could well utilise them in future to improve the efficiency of the fuel processing stages. An example of the HotModule fuel cell was on display.

Several different approaches to SOFCs were presented. Gerry Agnew (Rolls Royce Fuel Cell Systems, U.K.) described plans to build multi-MW systems integrated with gas turbines to form a 1 MW hybrid. Under an EU ‘Fifth Framework Programme’, it is intended to demonstrate a multi-kW stack test rig. Effort to date has concentrated on developing manufacturing techniques for low-cost ceramic components stable at high temperatures (900°C).

In contrast, Brian Borglum explained that Global Thermoelectric Inc. has focused on low-cost, intermediate temperature (750°C) planar anode-supported technology for their SOFCs. Their main effort has been to develop a 2 kW class prototype operating on reformed natural gas. Five of their RP-2 units have operated for 20,000 hours in 2002 to 2003 and have demonstrated peak net electrical efficiencies of 29%. Their next generation prototype is expected to yield an electrical efficiency of 30–35%, and fuel utilisation of 60–80%.

Nigel Brandon (Imperial College, London) provided details of intermediate temperature SOFCs, capable of operating at 500–600°C, that enable the extensive use of stainless steel components. The technology developed at Imperial College has been spun out into a venture company – Ceres Power Ltd. – for commercial exploitation. Markets being addressed are those needing 1–25 kW units combined heat and power, auxiliary and uninterruptible power units.

**The Poster Session**

A record 144 posters were displayed at the Symposium, and four of these were selected to receive prizes. Most of the oral papers and many of the posters will be published as a special edition of the *Journal of Power Sources*.

**Conclusion**

The technical feasibility of fuel cells has been widely demonstrated in extensive trials in numerous stationary and mobile applications. The industry is rapidly developing, with increasing numbers of companies supplying materials, components and balance of plant as well as building fuel cell stacks and devices utilising them. This parallels the initial developments of the motor industry where early pioneers were forced to design and fabricate every part, whereas nowadays modern vehicle assemblers are able to source components from competing specialists. This pattern will be a key factor in making fuel cells fully competitive with existing power plants. The fuel cell industry also needs to familiarise the public with the technology, and the rapidly increasing number of demonstration programmes will help in this.

**References**


**The Author**

Don Cameron is an Independent Consultant on the technology of fuel cells and electrolyser. He is a member of several Working Groups of the International Electrotechnical Commission, Technical Committee 105 on fuel cell standards, and is Secretary of the Grove Symposium Steering Committee.
ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Synthesis and Characterization of a New Modification of PIAI

A new PtAl phase (I), which is stable at room temperature under oxidising conditions, was synthesised at 200°C and 5 MPa. *In situ* high-temperature XRD experiments in air were performed to study the thermal behaviour of (I). At 400–700°C, Pt₃Al decomposes into Pt and Al₂O₃.

Oxidation of FePt Nanoparticles

Monodispersed FePt nanoparticles were synthesised using the airless operation technique based on the decomposition of Fe(CO)₅ and reduction of Pt acetylacetonate. The particle solution was then washed and subsequently deposited onto a thermally oxidised Si substrate. Nanoparticle assemblies were formed after solvent evaporation. The samples were heat-treated using rapid thermal annealing at 650°C for 30 min, in Ar with < 1 ppm of O₂. Oxidation has to be avoided to obtain the FePt L₁₀ phase. If O₂ is present, phases such as FePt₅, Fe₃O₄ and Pt form.

Ferromagnetism of FePt Nanoparticles Induced by Ion-Beam Irradiation

Both epitaxial and polycrystalline FePt films were grown in the chemically ordered L₁₀ phase and were non-magnetic at room temperature. Upon irradiation with 700 keV N⁺ ions at a dose of 1 × 10¹⁶ ions cm⁻² the chemical order was destroyed and ferromagnetism was induced.

Analysis of Surface and Bulk Behavior in Ni–Pd Alloys

The Bozzolo–Ferrante–Smith method was used to study Ni–Pd alloy surfaces. Large-scale atomistic simulations were performed to investigate surface segregation profiles as a function of temperature, crystal face and composition. Pd enrichment of the first layer was observed in (1 1 1) and (1 0 0) surfaces, and enrichment of the top two layers occurred for (1 1 0) surfaces. In all cases, the segregation profile showed alternate planes enriched and depleted in Pd. A weak ordering tendency was observed at low temperatures.

CHEMICAL COMPOUNDS

Unexpected Effect of Cyclodextrins on Water-Soluble Rhodium Complexes

[HRh(CO)₅{(p-µ-BuC₆H₅)P(m-C₆H₄SO₃Na)_2}₃] can be partially converted in the presence of β-cyclodextrin or randomly methylated β-cyclodextrin into the HO complex [HORh(CO)₅{(p-µ-BuC₆H₅)P(m-C₆H₄SO₃Na)_2}₃], under N₂, or to the hydrido complex [HRh(CO)₅{(p-µ-BuC₆H₅)P(m-C₆H₄SO₃Na)_2}]₂, under CO. No such effect was shown by [HRh(CO)₅{(p-µ-C₆H₄SO₃Na)_2}₃].

ELECTROCHEMISTRY

Kinetics and Mechanism of the Oxidation of Sodium Dithionite at a Platinum Electrode in Alkaline Solution

The oxidation of Na dithionite (I) in alkaline solution was studied by CV at a stationary and rotating Pt disc electrode. The reaction proceeds in two steps, with sulfate as a relatively stable intermediate and sulfate as a final product. The kinetics of the oxidation wave show a reaction order of 0.5 with respect to (I).

PHOTOCONVERSION

Imaging of Catalytic Activity of Platinum on p-InP for Photocathodical Hydrogen Evolution

Pt was deposited photocathodically on single-crystalline p-InP from aqueous H₃PtCl₆. Subsequent spatially resolved photocurrent measurements in H₂SO₄ at different potentials and comparison with optical micrographs of the Pt deposits showed that the catalytically most active deposits were formed at low light intensity (45 mW cm⁻²) and relatively negative potentials (–0.3 vs. SCE).

Orientation-Dependent Phosphorescence from Nanocrystals of Platinum Tetrathienylporphyrin Grown on Alkali Halides

Epitaxially oriented nanocrystals of PtTTP (1) were grown by vapour deposition on a cleaved surface of K halide single crystals. (1), deposited on the KCl (0 0 1) surface kept at 200°C, formed pyramidal crystals showing red phosphorescence. However, (1) deposited on the KBr (0 0 1) surface kept at 200°C formed plate-like crystals (2). The monoclinic molecular packing in (2) gave phosphorescence quenching.
**ELECTRODEPOSITION AND SURFACE COATINGS**

Investigation of the Interfacial Structure of Ultra-Thin Platinum Film Deposited by Cathodic–Arc


Ultrathin films of Pt (1) (15–65 Å) were deposited on Si substrates, using cathodic-arc deposition (2). The structure of the deposited (1) was found to consist of 3 layers: the Pt film, a Si oxide layer and a Pt silicide layer. In contrast to DC magnetron and electron beam deposited films, the silicide layer of (1) has a higher density and greater thickness. This is attributed to the higher energy of this deposition process. The attributes of (1) suggest that (2) is only suitable for producing mirrors of materials that do not react with each other, such as Pt and SiO₂.

**Synthesis and Characterization of Fe₁₀₀₋₇₄Pt₇₄ Alloy Thin Films**


The title films (1) with various Pt compositions (x = 15, 24, 46 and 78 at.%) were synthesised by magnetron sputtering. The XRD patterns of as-deposited (1) with all compositions exhibited a disordered phase with f.c.c. structure. Annealing of Fe₇₄Pt₂₆ films at high temperatures yielded an ordered L₁₀ phase with f.c.t. structure. DSC studies revealed exothermic peaks for phase transformation in different alloy compositions. The activation energies for phase transformations of (1) were found to increase with Pt concentration.

**Enhanced Hydrogen Sorption Capacities and Kinetics of Mg,Ni Alloys by Ball-Milling with Carbon and Pd Coating**


Mg₅Ni–C composites (1) were prepared by ball-milling the Mg,Ni alloy in the presence of pregound graphite and Pd-coated Mg,Ni alloy powders were obtained by controlled chemical deposition of Pd on the alloy surface. Optimised pregrinding of C enhances the H₂ desorption capacity of (1) to 2.6 wt.% at 150°C. Pd deposition raises it further to 2.8 wt.%.

**Electrochemical Synthesis of Zeolite-Like Ruthenium-Based Hexayanometalates Multi-Film Assemblies**


CV was used to synthesise zeolite-like films of K₃₂Ru₂[Fe(CN)₆]₃ (RF) or Ru hexacyanoferrate and K₃₂Ru₂[Ru(CN)₆]₃ (RR) or Ru hexacyanoruthenate. Formation of porous multi-film assemblies of Prussian blue (PB) over RF was achieved by either direct electrodeposition of PB over RF or RF over PB during repetitive potential cycling, or by electrochemically driven insertion–substitution methods.

**HETEROGENEOUS CATALYSIS**

Ethylene Production Using a Pd and Ag–Pd–Y-Zeolite Catalyst in a DC Plasma Reactor


The addition of Pd to a NaOH-treated zeolite in a DC plasma reactor, using a feed of CH₄, H₂ and O₂ (< 2.5%), gives the same CH₂ conversion of 20–60% as the reactor without the Pd. However the initial acetylene produced is selectively hydrogenated in situ to ethylene. The catalyst is most selective ~ 45°C, where it produces ethylene:ethane of ~ 4:1 with no acetylene. Further increases in selectivity and operating temperature were achieved by adding Ag. The system has achieved ethylene yields as high as 30%, with H₂ yields of 40% and little production of the combustion products CO₂ and H₂O.

Solvent-Free Pd-Catalysed N-Arylation of Amines, Amides and Diaza-18-Crown-6


The N-arylation of amines, amides and diaza-18-crown-6 with weakly activated aryl bromides catalysed by Pd²⁺/L₆ and the arylation of 2-pyrrolidone with 2-bromothiophene catalysed by CuI/1,2-di(methylamino)cyclohexane were performed without solvent at 60–100°C. The addition of graphite prevents caking of the reaction mixture. The arylation products were obtained in good yields (60–78%).

Synthesis and Characterization of PalladiumContaining Membranes Based upon Polyacrylic Acid


Porous catalytic membranes were prepared by crosslinking polyacrylic acid dispersions with a bifunctional crosslinker in the presence of Pd particles. Pd nanoparticles, stabilised with polystyrene-block-polyethyleneoxide, were immobilised in the polymer network in different ways. The polymer/Pd network was prepared as thin flat membranes and dried, retaining the porosity and 3D network structure. Different reduction and preparation methods were used to obtain differences in particle size and distribution of the Pd.

Ir/SiO₂ as a Highly Active Catalyst for the Selective Reduction of NO with CO in the Presence of O₂ and SO₂


SiO₂-supported Pt, Rh, Pd and Ir catalysts were prepared by impregnating SiO₂ with aqueous solutions of their salts. Ir/Al₂O₃ was also prepared. Ir/SiO₂ gave excellent activity with respect to NO reduction with CO in the presence of O₂ and SO₂. This could be due to the formation of a dir-type coordinated species of NO and CO to one Ir atom, a possible reaction intermediate in the formation of N₂.
The Os/Cu–Al-Hydrotalcite Catalysed Hydroxylation of Alkenes
H. B. FRIEDRICH, M. GOZNER, X. MAHOB, T. D. NGOBO
Os/Cu–Al-hydrotalcite (1) was prepared by precipitation with N-methylmorpholine oxide as oxidant. (1) heterogeneously catalyses the hydroxylation of olefins to give diols selectively and in high yield. Heat-treating (1) initially has a beneficial effect, with 200°C being the optimal temperature. (1) calcined at 200°C reacted faster than uncalcined (1). Os does not leach into the reaction solution.

Scope, Kinetics, and Mechanistic Aspects of Aerobic Oxidations Catalyzed by Ruthenium Supported on Alumina
Ru/Al2O3 (1) was obtained by modification of the preparation of Ru(OH)2·nH2O. (1) showed high activity for the oxidation of activated, nonactivated, and heterocyclic alcohols, diols, and amines at 1 atm of O2. (1) could be reused seven times without a loss of catalytic activity and selectivity for the oxidation of benzyl alcohol. The oxidation proceeds through an alcoholate/β-hydride elimination mechanism. The β-hydride elimination is a rate-limiting step.

HOMOGENEOUS CATALYSIS
Additive Effects in Palladium–Indium Mediated Barbier Type Allylations
L. A. T. CLEGHORN, L. R. COOPER, R. GRIGG, W. S. MACLACHLAN
The effect of adding various amines (1 equiv.) or Cul (0.2 equiv.) to a Pd/In bimetallic cascade reaction was examined. In the class 1 cascade reaction of aldehydes, aryl iodides and allene, generating homoalylalcoholic acids, the reaction time was reduced from 16 to 2 h. This was accompanied by an impressive increase in yield. The amine additives aid the solvation of the In powder (accelerating the rate of transmetallation) and protect the catalytically active Pd species. All the cyclic amines improved yield.

Assignment of the Structure of a Ru(II)–BINAP Catalyst
A Ru(II)–BINAP catalyst (1) was prepared from cyclooctadienyl Ru dichloride and (R)-BINAP in the presence of triethylamine. The reaction was carried out in toluene at reflux. The structure of (1) was identified using NMR spectroscopy as the diethylmammonium salt ([C5H5]2NH4)2RuCl2[(R)-BINAP]2. Due to the saturated octahedral environment of (1), activation of (1) with acid is necessary to allow low pressure (40 psi) and low temperature (40°C) catalytic hydrogenation reactions.

FUEL CELLS
Composite Electrodes Made of Pt Nanoparticles Deposited on Carbon Nanotubes Grown on Fuel Cell Backings
Multiwalled C nanotubes (MWCNTs), with typical lengths of 20 µm and diameters of 40 nm, were grown directly on C paper backing. A sulfonic acid–silicate intermediate was used to deposit Pt nanoparticles on the MWCNTs in order to obtain an electrode for electrocatalysis. CV showed that there is electrical contact through the MWCNTs between the Pt particles and the C paper backing.

Electro-Oxidation of Methanol and Ethanol on Poly(3,4-Ethyleneoxythiophene) with Dispersed Pt, Pt + Sn, and Pt + Pb Particles
Sn and Pb additives were found to increase the catalytic activity of Pt particles dispersed on a PEDT layer deposited on Au or steel towards anodic oxidation of MeOH and EtOH. In the presence of Sn, the steady-state current density of MeOH oxidation increases ~ × 100, while Pb only promotes the Pt catalyst activity by ~ × 2. The Sn promotion effect may be due to a homogeneous catalytic reaction with the Sn(IV) and Sn(II) ions participating as mediators.

Modeling the Electro-Oxidation of CO and H2/CO on Pt, Ru, PtRu and PtSn
DFT calculations were used to describe the adsorption of H2, CO and H2O on the close packed surfaces of Pt, Ru, PtRu and PtSn. The calculated adsorption energetics were used in a model to describe the electro-oxidation of CO and H2 at conditions relevant to a PEMFC anode. The model showed that Ru, PtRu and PtSn begin to oxidise CO at lower potentials than Pt. PtRu was shown to have considerably lower overpotential for H2 oxidation in the presence of CO than Pt. PtSn was even better than PtRu, while Ru was considerably poorer than Pt.

Development of Residential PEFCCogeneration Systems: Ru Catalyst for CO Preferential Oxidation in Reformed Gas
A novel Ru/Al2O3 catalyst (1) was prepared by an impregnation method. The performance of (1) in a single-stage CO preferential oxidation removal reactor (2) was investigated for residential PEFC cogeneration systems. The outlet CO concentration of (2) was reduced to < 1 ppm even at [O2]/[CO] = 1.5. A natural gas fuel processor equipped with (2) achieved the target thermal efficiency of 77% (LHV).
NEW PATENTS

ELECTROCHEMISTRY

Water Electrolysis Cell
HONDA GIKEN KK * Japanese Appl. 2003-166,093
A water electrolysis cell (1) has a pair of catalytic layers (2) between which is a solid polymer electrolyte membrane. The catalyst in the anode side of (2) is made from a Ru-Ir alloy, and a metal(s) selected from Fe, Ni and Co, or an oxide of the alloy, or a mixture of alloy and oxide. At least one of Fe, Ni and Co has molar ratio w.r.t. Ru and Ir of 0.05–0.13 mol to 0.8–2.2 mol, preferably 1.8–2.2 mol of Ru and 0.8–1.2 mol of Ir. (1) gives a high energy efficiency over a long time.

PHOTOCONVERSION

Phosphorescent Dendrimers in LEDs
ISIS INNOVATION LTD * World Appl. 03/079,736
An LED comprises at least one layer containing a phosphorescent organometallic dendrimer with a metal cation, such as Ir, and two or more coordinating groups (1) as part of its core. At least two of (1) each have a dendron attached, and at least one of them comprises at least one N atom forming part of an aromatic ring system or directly bonded to at least two aromatic groups.

Photoelectrochemical Cell
NIPPON SHEET GLASS KK * Japanese Appl. 2003-163,037
An electrode for a dye sensitising-type photoelectrochemical cell of low internal resistance has a TiO₂ porous semiconductor body that includes a dye sensitising agent (1) and a conductive whisker (2). (1) is a bipyridine-carboxylic acid Ru complex hydrate and (2) is preferably of diameter 0.4–0.7 μm, length 5–20 μm, aspect ratio 10 to 20 and resistance 0.1–1 Ω cm⁻¹. The cell has little power generation loss.

Organic Electroluminescent Iridium Complex
MITSUBISHI CHEM. CORP * Japanese Appl. 2003-192,691
An organic electroluminescent element (1) has a luminescent layer containing a mixed ligand-type organic Ir complex (2) sandwiched between an anode and a cathode. (2) gives improved colour purity in the emission of light of long wavelength, has high luminescent efficiency and gives long life to (1).

ELECTRODEPOSITION AND SURFACE COATINGS

Iridium-Aluminium Protective Surface Coating
GENERAL ELECTRIC CO * U.S Patent 6,630,250
An article substrate is protected by a coating over its surface formed by depositing a layer of Ir, then a layer of Al on top of the Ir layer. The substrate, Ir layer and Al layer are then heated and form an Ir-Al protective coating. A ceramic thermal barrier coating may be applied over the protective coating.

APPARATUS AND TECHNIQUE

Biosensor for Detecting Macromolecular Biopolymers
INFINEON TECHNOLOG AG * World Appl. 03/079,016
Macromolecular biopolymers can be detected by a sensor that contains a unit to immobilise them and a unit to detect their signal. The latter unit uses a Pd, Pt, Au, etc., electrode. An evaluation circuit for the signal, containing a semiconducting layer with an organic material, is coupled to the detection unit.

Optical Sensor for Detecting an Analyte
METTLER TOLEDO GmbH * U.S Patent 6,653,148
An optical sensor (1) for determining an analyte, specifically O₂, has a sensor matrix (2) made of a fluoropolymer. (2) contains a luminescent indicator with a metal complex of Ru, Rh, Ir or Re, and with at least one partially fluorinated ligand. Detection occurs by bringing (1) into contact with the measuring medium and by determining changes in an optical property resulting from interaction between the analyte and the luminescent indicator.

HETEROGENEOUS CATALYSIS

Catalyst for the Synthesis of Chiral Vicinal Diols
CSIR * European Appl. 1,346,767
A multifunctional reusable catalyst M-(S), made on support (S) produces chiral vicinal diols by tandem and/or simultaneous reactions involving Heck coupling, N-oxidation and addition reaction of olefins in the presence of cinchona alkaloid compounds in a single pot. (S) is a layered double hydroxide (LDH), resin, SiO₂, etc., or unmodified support selected from resin and SiO₂. M is an active species of ≥ 2 of Pd, Ru, Os, W. M-(S) is PdOs-LDH, PdOsW-SiO₂, etc., and is used in place of soluble Os catalysts.

Treatment of Industrial Organic Pollutants
CNRS * World Appl. 03/064,333
Industrial effluent containing organic pollutants is treated by ozonation in a reactor in the presence of a Ru and/or Ir catalyst (1) supported on CeO₂, ZrO₂ and/or TiO₂. Catalyst particle size is 20–500 μm. The effluent treated with ozone and the catalyst is continuously fed through a separation system to separate (1). Part of the effluent free of (1) is removed; the remainder is recycled with (1) into the reactor.

Production of Amines
BASF AG * World Appl. 03/066,571
Amines are produced by the catalytic hydrogenation of nitroaromatics. The C supported catalyst of Pt, Pd and/or Ir is then separated from the reaction mixture which contains aromatic amine(s) and H₂O. The catalysts are separated by membrane filtration at 5–50 bar on the side of the suspension (1), a difference in pressure between (1) and the side of the permeate of ≥ 0.3 bar, and a flow rate of 1–6 m s⁻¹ on (1).
Catalyst for the Reduction of NO to N₂

Palladium and Zirconia Catalyst

A catalyst (1) contains Pt crystals in contact with a mixture of MgO and CeO₂ or Pt/MgO-CeO₂ (2) which was selectively sulfated. (1) has excellent activity, selectivity and stability for reducing NO to N₂ using H₂ as a reducing agent, at 100–200°C and in an excess of O₂ (5 vol.%), H₂O (5 vol.%) and/or SO₂ (20 ppm). With (2), full NO conversion and 83% N₂ selectivity are obtained at 150°C with a reaction mixture of 0.25% NO/1% H₂/5% O₂/5% H₂O/He.

Production of 7-Alkyl-8-hydroxyquinolines

7-Alkyl-8-hydroxyquinolines (1) are produced in high purity and good yield by reducing 7-alkenyl-8-hydroxyquinolines under H₂ in the presence of an inorganic base, such as NaOH, and a Group VIII metal catalyst, such as Pd, Pd/C, etc. No substantial hydrogenation of the hetero-ring occurs so an adequate reaction rate can be obtained. (1) find use as an extracting agent for solvent extraction of metal ions.

Multiple-Component Metallic Combustion Catalyst

Residual and lighter distillate fuels are used with greater efficiency by using low concentrations of specific bimetallic or trimetallic fuel-borne catalysts, such as a fuel-soluble Pt with Ce and/or Fe catalyst (1). (1) reduces the fouling of heat transfer surfaces by unburned C while limiting the amount of secondary additive ash. Ultra-low levels of this nontoxic metal combustion catalyst are used to improve heat recovery and lower emissions of the pollutants.

 Palladium and Zirconia Catalyst

A catalyst which includes Pd and Zr is formed as a suspension (1) and can be coated onto a metal strip. (1) is formed by combining Pd nitrate with a solution of an alkyl ammonium hydroxide, and further mixing with a hydrous Zr oxide. HNO₃ may be added to the Pd nitrate. The resulting composition exhibits superior activity and good adhesion to the metal strip, and can catalyse a combustion reaction as well as a steam reforming reaction.

Hydrogenolysis Catalyst

A hydrogenolysis catalyst (1) comprises: (a) a component(s) selected from Pd oxide, Pd oxide monohydrate, and Pd hydroxide in the Pd(II) oxidation state and contains 0.1–50 wt.% Pd, and (b) a component(s) from Pt, Ru, Rh, Ir and Au, on a non-organic porous support, such as activated C, acetylene black, SiO₂/Al₂O₃, TiO₂ and ZrO₂. (1) has high hydrogenolysis performance at low temperatures and during the debenzylation reaction of a compound wherein a benzyl group combines with a N atom. This is difficult for conventional catalysts.

Three-Way Catalysts

A Pt group metal (pgm) three-way catalyst contains a high temperature support (1) and a low temperature support (2), both with enhanced catalytic activity at >500°C and 200–400°C, respectively, and each being in the same washcoat layer. The mean particle size of (1) and (2) in the washcoat slurry is <20 μm to prevent formation of a solution or a sol with the liquid medium of the slurry. The pgm is impregnated into the support either after formation of the washcoat on a non-porous refractory, metallic or palletised substrate, or before forming the washcoat slurry.

HOMOGENEOUS CATALYSIS

Manufacture of Ketopantolactone

A process is described to oxidise pantolactone to ketopantolactone (1) with a periodate in the presence of a Ru catalyst in aqueous solvent using a microwave field. (1) is a key intermediate in the manufacture of pantothenic acid, a member of the B complex vitamins and a constituent of coenzyme A. The asymmetric hydrogenation of (1) yields D(-)-pantolactone for pantothenic acid manufacture.

Hydrogenation of Carboxylic Acids

A homogeneous process for the hydrogenation of carboxylic acids and/or their derivatives in the presence of a catalyst comprising Ru, Rh, Os, Pd or Fe and an organic phosphine is described. The hydrogenation is carried out in the presence of at least ~1 wt.% of H₂O. The catalyst can be regenerated in the presence of H₂ and H₂O.

Osmium-Assisted Oxidative Cleavage of Olefins

An Os-assisted process for oxidative cleavage of oxidisable organic compounds, such as unsaturated organic compounds: alkenes and olefins, uses an Os catalyst chosen from OsO₄, OsCl₅, K₂OsO₅₂H₂O, and a peroxo compound selected from peroxymonosulfuric acid and its salts. The C-C double bond of an organic compound can be oxidised to aldehyde, carboxylic acid, ester, etc., in a reaction that gives ozonolysis results but fewer problems. An aldehyde can thus be oxidised alone or with the Os in an interactive solvent to produce an ester or a carboxylic acid.

Ruthenium Metal Alkyldiene Complexes

Ru alkyldiene complex (PC₅)(L)Cl₂Ru(CHPh) catalysts, where L is a triazolylidene ligand, are more active for olefin metathesis at elevated temperatures than the parent (PC₅)Cl₂Ru(CHPh). (1). The complex with L = 1,3,4-triphenyl-4,5-dihydro-1H-triazol-5-ylidene (2) catalyses the RCM of substituted dienes to give tetrasubstituted cyclic olefins in good yield. (2) has the same stability towards O₂ and moisture as (1).
Carbonyl Compound Production
MITSUBISHI CHEM. CORP. Japanese Appl. 2003-171,372

A carbonyl compound is produced by the dehydrogenation of an alcohol in the presence of an organic phosphine-Ru complex catalyst. The catalyst is obtained by mixing an organic phosphine and a Ru compound in the atomic ratio P:Ru of 2–8, followed by heating. Addition of a H acceptor is not needed. Both the reaction rate and reaction efficiency are increased.

FUEL CELLS
Aerogel Pt-Ru-C Catalyst in DMFC
KOREA INST. SCI. TECHNOL. U.S. Appl. 2003/0,176,277

An aerogel-type catalyst (1) contains 5–70 wt.% Pt and Ru, remainder C. The Pt:Ru atomic ratio is 1:4 to 4:1. A DMFC that employs (1) as an anode catalyst is disclosed. (1) is manufactured via a sol-gel process by adding metal salts and a base catalyst to a solution of organic gel materials, further adding a solution of basic amine and adjusting the pH to form a sol. This is followed by ageing, supercritical drying to make a type of aerogel (2), carbonising (2) and H reduction.

Nano-Level Platinum/Carbon Electrolyst
T. LU, X. LI and W. XING U.S. Appl. 2003/0,224,926

A nano-level Pt/C electrolyst (1) for the cathode of fuel cells is prepared using the chloride, bromide or iodide of NH₄ or K as the anchoring agent for the H₃PtCl₄. The Pt particles are homogeneously distributed in the interstices and on surfaces of the active C. (1) has high specific activity per unit mass for the catalytic reduction of O₂.

Cell Unit of a Fuel Cell
SANYO ELECTRIC CO LTD Japanese Appl. 2003-151,577

A cell unit of a fuel cell has a cell structure consisting of a Pt catalyst layer (1) and a gas diffusion layer arranged, in that order, on both sides of an electrolyte layer (2). (2) consists of a proton-conductive gel and an interlayer (3) containing C particles and electrolyte material. The porosity of (3) is smaller than that of (1). Even when (2) is formed using sol-gel processing, the pores in the catalyst layer are not covered by the electrolyte material. Pt utilisation in the catalyst is therefore increased and a high battery performance is obtained since the reaction gas is being fully supplied to the catalyst layer.

Fuel Cell Catalyst
HONDA GIKEN KOGYO KK Japanese Appl. 2003-173,787

A fuel cell, with an ion exchange membrane arranged between a negative and a positive electrode, generates power by contact of H₂ with the fuel cell catalyst contained in the negative electrode. At the same time O₂ contacts the catalyst in the positive electrode. The catalyst contains Pt alloyed with Fe, Co and/or Ni or other elements from Group VIII and Al. The catalyst can be easily structured and its catalytic function is as high or higher than that of Pt.

ELECTRICAL AND ELECTRONIC ENGINEERING
Multilayer Perpendicular Media
SEAGATE TECHNOLOG. LLC World Appl. 03/083,839

C or B is added into the Co/Cr layers of a multilayer perpendicular magnetic media (1) structure to reduce media noise. The structure of (1) has sharp interfaces between the Co-alloy layers and Pd or Pt layers, and significantly reduces exchange coupling. This relates to magnetic recording, especially to multilayer media that have columnar microstructure, and provides improved exchange decoupling and reduced noise.

Ruthenium Metal Layer
MICRON TECHNOLOG. INC. U.S. Patent 6,617,248

A Ru metal layer for semiconductors is prepared by combining a Ru precursor with a measured amount of O₂ to form a Ru oxide (1) layer. (1) is annealed in H₂-rich gas to react the O in (1) with H₂. By varying the O₂ flow rate during the formation of (1), a Ru metal layer can be formed with various degrees of smooth and rough textures. The method reduces problems associated with manufacturing semiconductor devices, particularly in forming a Ru metal layer.

Synthetic Free Layer Structure for MRAM Devices
MAXTOR CORP U.S. Patent 6,649,960

A MRAM cell includes: a bottom electrode layer, a magnetic reference layer (1), an insulating layer, a synthetic free layer (2), and a top electrode layer. (2) has a first magnetic layer (3), a Ru antiferromagnetic coupling layer, and a second magnetic layer (4). (1), (3) and (4) are made of magnetic material, such as CoFeB, CoFe, or a bilayer of NiFe and CoFe. Layer (3) is made thicker than layer (4) for better operation.

Manufacture of Semiconductor Devices
HITACHI LTD Japanese Appl. 2003-158,203

A method for manufacturing a semiconductor device that can etch a Ru film (1) with good reproducibility and at the same time achieve the high etching selection ratio of a resist film is claimed. The method comprises forming a resist pattern on (1), then irradiating its surface with an UV ray in a pretreatment chamber within an etching unit to remove any organic contaminant adhered to its surface. (1) is then etched, using the resist pattern as a mask, in an ozone atmosphere inside the etching unit.

Capacitor for a Semiconductor Device
HYNIX SEMICOND. INC. Japanese Appl. 2003-163,284

A semiconductor device includes a diffusion barrier layer (1) containing a ternary system of Ru, Ti and O formed by MOCVD on a substrate. A capacitor formed on (1) includes a bottom electrode formed on (1), a dielectric layer (2) formed on the bottom electrode, and a top electrode formed on (2). (1) prevents capacitor malfunction by suppressing O diffusion.
Effects of Oil Additives on Autocatalysts

Since the introduction of autocatalysts in the 1970s, the effects of sulfated ash, phosphorus and sulfur (SAPS) in engine oils on catalyst performance and durability have been continuously monitored. However, the deterioration in emissions attributable to the oil can be difficult to quantify. Sulfated ash in oils derives from the salts of alkali and alkaline earth metal detergent additives. These help to keep engine surfaces free of combustion deposits. There is also a contribution from the ZDDP (zinc dialkyldithiophosphate) antwear, antioxidant agents in the oil (1).

The chief concern over ash levels in oil is that in diesel-engined vehicles non-combustible ash deposits become trapped in the channels of diesel particulate filters. These cause an increase in the back pressure over the filter, which can potentially affect engine performance. The sulfur in engine oils originates from the additive components and the oil base stock. As the amount of sulfur in fuel is being reduced to very low levels there is concern that sulfur in the oil will become more important and it remains a consideration for NOx-traps fitted to lean-burn engines. Oil sulfur has also been shown to contribute to particulate matter (PM) in heavy-duty diesel engines fitted with oxidation catalysts, resulting in failure to meet defined emission limits in some instances.

Many studies have been published examining the effects on gasoline catalyst activity of phosphorus level (from ZDDP) and detergent components, such as calcium, in the engine oils, but there is less published work for diesel catalysts. If compounds such as zinc pyrophosphates (from ZDDP) are deposited on a catalyst they can form a diffusion barrier preventing exhaust gas molecules reaching active sites. The studies were often performed with bench engines and extended ageing was simulated. This was done by passing oil through the engine in a short time period (for example, 100 hours) equivalent to the amount which would have been consumed in 80,000 km of road driving (ageing) by a vehicle. The fuel was doped with lubricating oil and the mixture combusted in the engine. In some cases the engine inlet valve seals were removed to increase oil consumption. The studies generally showed that phosphorus reduced catalyst activity and that increased phosphorus levels enhanced deactivation. However, increasing the ratio of alkaline earth metal to phosphorus decreased the quantity of phosphorus deposited on the catalyst.

Concerns have been expressed that such studies do not simulate real world deactivation because of the accelerated oil consumption, operation at fixed engine speed/load conditions and non-representative means of oil consumption. However, there are further aspects that influence vehicle fleet studies, such as thermal deactivation, shifts in oxygen response characteristics and other engine calibration factors over time, as well as differences in the levels of phosphorus deposition on the catalyst. A few of the vehicle trial results have been published and all conclude that although the vehicles have invariably met the emission limits for which they were designed, the non-destructive removal of phosphorus noticeably improves catalyst performance, especially light-off.

With severer emission limits under discussion, together with extended durability requirements, the impact of SAPS on catalysts and filters is increasing the need to develop low SAPS oils that do not compromise engine wear or oil consumption. The oil additives industry is actively pursuing this, and may ultimately require the availability of ashless, phosphorus- and/or sulfur-free components and the use of higher quality, low-sulfur base stocks, all of which adds complexity and cost to the formulations.

A. J. J. Wilkins

Reference


Tony Wilkins is a former Technology Development Manager in Johnson Matthey’s Catalytic Systems Division (now ECT, Johnson Matthey Catalysts). His long experience of the autocatalyst industry gives him a breadth of insight into the changing technology and its complexities.