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Transport and the Environment
PROGRESS TO DATE AND THE REMAINING CHALLENGES

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Across the entire globe, motor vehicle usage has increased tremendously in recent years. In 1950, there were about 53 million cars on the world's roads; only four decades later, the global automobile fleet is now over 430 million, more than an eightfold increase. On average, the fleet has grown by about 9.5 million automobiles per year over this period. Simultaneously, as illustrated in Figure 1, the truck and bus fleet has been growing by about 3.6 million vehicles per year (1). If the approximately 100 million two-wheeled vehicles around the world is included, a number that has been growing at about 4 million vehicles per year over the last decade, the global motor vehicle fleet is now approximately 675 million.

Simultaneously, over the course of the past two decades, substantial progress has been made in reducing emissions from vehicles. North America, Europe and Japan have developed significant motor vehicle pollution control programmes which have led to tremendous advances in petrol car control technologies. At present, similar technologies are under intensive development for diesel cars and trucks, and significant breakthroughs are starting to appear with production diesel vehicles. As a result of these efforts around the world, motor vehicle emissions today are much lower than they might otherwise have been. Based on global emissions under standardised test conditions, it is estimated that carbon monoxide, hydrocarbons and nitrogen oxides emissions are, respectively 90, 63 and 51 per cent lower around the world than they would have been if countries had not moved forward on motor vehicle emission controls. In urban areas, under conditions which give rise to the highest levels of ozone or carbon monoxide in the air, actual reductions have been much lower. None the less, most of the gain has been the result of the introduction of platinum based catalytic converters.

However, in many areas, the air quality problem remains serious and widespread, and motor vehicles continue to be the dominant source of the emissions which cause many of these problems. Air pollution problems which are related to motor vehicles are no longer limited to the countries in the Organisation for Economic Co-operation and Development (OECD); areas of rapid industrialisation are now starting to note similar air pollution problems to those of the industrialised world. Cities such as Mexico, Delhi, Seoul, Singapore, Hong Kong, São Paulo, Manila, Santiago, Bangkok, Taipei and Beijing, to cite just a few, already experience unacceptable air quality, or are projecting that they will do so in the relatively near future.

Furthermore, the number of vehicles continues to grow. Because of this continued growth, on top of the existing air pollution problems which still plague most countries, additional control initiatives will have to be undertaken to attain clean, healthy air.

Environmental Problems Caused by Motor Vehicle Emissions

Initially, the problems resulting from motor vehicle emissions were most apparent in city centres, but recently lakes and streams and even remote forests have also experienced significant degradation. Carbon monoxide, hydrocarbons and nitrogen oxides emitted by motor vehicles are also contributing to global atmospheric changes which most scientists believe are likely to alter the climate of the planet. Nevertheless, the primary greenhouse gas remains carbon dioxide, produced by motor vehicles and from other sources. Although detailed discussion of this pollutant is beyond
Fig. 1 In the last four decades the number of cars in use throughout the world has increased more than eightfold. During this period truck and bus fleets have also increased steadily, while an increase in two-wheeled vehicles has occurred in the last decade.

Pollutants in Urban Areas

Over 90 per cent of the carbon monoxide emitted in cities generally comes from motor vehicles. People with coronary artery disease who are exposed to carbon monoxide during exercise experience chest pain (angina); exposure also alters their electrocardiograms (2). In addition, foetuses, people with sickle cell anaemia and young children are also highly susceptible to exposure to low levels of carbon monoxide. Although ambient carbon monoxide levels have been reduced across Europe, Japan, and the United States of America, the problem is far from under control (3). Global carbon monoxide concentrations in the lower atmosphere are increasing by 0.8 to 1.4 per cent per year (4).

Nitrogen oxides emissions from vehicles and other sources produce a variety of adverse health and environmental effects. They react chemically with hydrocarbons to form ozone and other highly toxic pollutants (5). Next to sulphur dioxide, nitrogen oxides emissions are the most prominent pollutants contributing to acidic deposition. Direct exposure to nitrogen dioxide leads to increased susceptibility to respiratory infection, increased airway resistance in asthmatics, and decreased pulmonary function. Short term exposure to nitrogen dioxide has resulted in a wide ranging group of respiratory problems in school children, among the most common are coughs, runny noses and sore throats, and also to increased sensitivity to urban dust and pollen by asthmatics. Some scientists believe that nitrogen oxides are significant contributors to the dying forests seen throughout central Europe.

Because lead is added to petrol, motor vehicles have been the major source of lead in the air of most cities. Several studies have now shown that children with high levels of lead accumulated in their baby teeth experience more behavioural problems, lower IQ and decreased ability to concentrate. Most recently, in a study of 249 children from birth to two years of age, it was found that those with prenatal umbilical-cord blood lead levels at or above 10 micrograms per decilitre consistently scored lower on standard intelligence tests than those having lower lead levels. As a result the U.S. Department of Health and Human Services considers all children at levels above 10 micrograms per decilitre of lead in their blood to be at risk (6).

Other toxic emissions from mobile sources are also a serious problem. A variety of studies has found that in individual metropolitan areas, mobile sources are one of the most important, possibly the most important, source category in terms of their contribution to health risks associated with air toxicity. For example, according to the U.S. Environmental Protection...
Agency, mobile sources are responsible for approximately 58 per cent of the air pollution related cancer cases in the U.S.A. each year.

Regional Considerations

The most widespread air pollution problem in areas with temperate climates is ozone, one of the photochemical oxidants which results from the reaction of nitrogen oxides and hydrocarbons in sunlight (7). Many individuals exposed to ozone suffer eye irritation, cough and chest discomfort, headaches, upper respiratory illness, increased asthma attacks, and reduced pulmonary function (8).

Numerous studies have also demonstrated that photochemical pollutants inflict damage on forest ecosystems and seriously affect the growth of certain crops.

Although ozone in the lower atmosphere does not come directly from motor vehicles, they are the major source of the ozone precursors, hydrocarbons and nitrogen oxides, throughout the industrialised world. Over the past 100 years, "background" ozone levels have approximately doubled (9), and monitoring data suggest that ozone concentrations are increasing by about 1 per cent per year in the northern hemisphere (10).

Acid deposition results from the chemical transformation and transport of sulphur dioxide and nitrogen oxides. Evidence indicates that the role of nitrogen oxides may be of increasing significance with regard to this problem.

Global Changes

A significant environmental development during the 1980s was the emergence of global warming, or the greenhouse effect, as a matter of major international concern. Pollutants associated with motor vehicle use can increase global warming by changing the chemistry in the atmosphere so as to reduce the ability of the sun's reflected rays to escape. As noted by the Intergovernmental Panel on Climate Change, "Increases in CH₄, NMHCs, and CO all lead to increases in O₃, and decreases in OH, thus leading to an increase in radiative forcing." (11)

It is important to note that the available evidence indicates that emissions of nitrous oxide, a potent greenhouse gas, tend to increase with the use of three-way catalytic converters. Based on a review of available literature as well as some new testing on nine vehicles, General Motors Research has concluded that vehicular emissions of nitrous oxide are about 125Gg in the U.S.A. and about 200Gg worldwide. "Based on this value and the rate of N₂O increase in the stratosphere, vehicles in the United States emit about two percent of anthropogenic N₂O emissions and contribute only 0.1 per cent of the calculated temperature increase from greenhouse gases." (12)

The State of the Urban Environment

The Example of Asia

As noted earlier, motor vehicle related pollution problems are not limited to the highly industrialised West. As a result of the large and growing number of poorly maintained vehicles, with minimal, if any, pollution controls, and powered by unusually dirty fuels, most major cities of Asia are already experiencing serious motor vehicle related air pollution problems, frequently on top of other serious environmental insults. In virtually every city for which data is available, carbon monoxide, lead and particulate, coming primarily from road traffic, exceeds acceptable norms. Further, vehicles contribute significant amounts of hydrocarbons and nitrogen oxides emissions, which are frequently toxic as well as contributing to photochemical smog in cities with the appropriate meteorological conditions.

In Thailand, for example, the Office of the National Environment Board has monitored levels of carbon monoxide, particulate matter and lead near major roads in Bangkok since 1984. According to their latest annual report the "air pollution problem in Thailand is serious near the major streets." (13) In certain areas of the city where traffic density is high, "particulate matter's concentrations far exceed the daily ambient air quality standards of 330 microgram/cubic meter on any day, and are as high as 2–3 times standard values on some
days”. Carbon monoxide levels are also high in some areas of high traffic density, frequently exceeding air quality standards.

A study of blood lead levels of policemen exposed to three different rates of vehicular traffic, found a positive and statistically significant link between traffic exposure and blood lead levels (14).

In Hong Kong, approximately “1.5 to 2 million people are exposed to unacceptable levels of sulphur dioxide and nitrogen dioxide and about three million people are exposed to high particulate levels. Many people are exposed to unacceptable levels of all three pollutants.” (15) “The most common adverse health effects of these pollutants take the form of increased incidence of respiratory illnesses, such as asthma and bronchitis. The high levels of air pollution in many parts of Hong Kong must seriously aggravate the condition of those already suffering from such illnesses and contribute to the onset of chronic conditions. Other health effects such as lung cancer can be caused by air pollution, as certain air pollutants, such as those emitted from diesel vehicles, are known to be carcinogenic.” (15)

The air pollution problem in many urban areas is compounded by the life style and climate in many of the warmer Asian cities. As a result there is much greater public exposure to the emissions from vehicles which are emitted directly at the breathing zones of many millions of people. This was reinforced in a recent study conducted by the East West Center where an individual carried a personal exposure monitor throughout the day (16). Carbon monoxide levels were found to increase dramatically during a vehicle trip compared to levels in a house, even when a charcoal stove was in use.

**International Progress in Controlling Pollution**

Advances in automotive technologies have made it possible to lower emissions from motor vehicles dramatically. Increasingly, countries around the world have been taking advantage of these technologies. Initial crankcase hydrocarbon controls were first introduced in the early 1960s followed by exhaust carbon monoxide and hydrocarbons standards later that decade. By the early to mid 1970s most major industrial countries had initiated some level of vehicle pollution control programme.

During the mid to late 1970s, advanced technologies were introduced on most new cars in the U.S.A. and Japan. These technologies resulted from a conscious decision to “force” the development of new approaches, and were able to reduce dramatically carbon monoxide, hydrocarbons and nitrogen oxides emissions, to levels unachievable by previous systems. As knowledge of these technological developments on cars spread, and as the adverse effects of motor vehicle pollution became more widely recognised, more and more people across the globe began demanding the use of these systems in their countries. During the mid 1980s, Austria, the Netherlands, and the Federal Republic of Germany adopted innovative economic incentives to encourage purchase of low pollution vehicles. Australia, Canada, Finland, Austria, Norway, Sweden, Denmark and Switzerland all decided to adopt mandatory requirements. Even rapidly industrialising, developing countries such as Brazil, Chile, Taiwan, Hong Kong, Mexico, Singapore and South Korea have adopted stringent emissions regulations.

After years of debate, the European Community has also made significant strides. As 1990 came to a close, the European Council of Environmental Ministers reached unanimous agreement to require all new models of light duty vehicles, by 1992/1993, to meet emission standards sufficiently stringent to require the universal use of catalytic converters based upon platinum group metals on all petrol fuelled vehicles. Further, they voted to require the Commission to develop a proposal before 31 December 1992 which, taking account of technical progress, will require a further reduction in limits. Presumably this proposal should be roughly equivalent to U.S. standards of 0.25 grams per mile non-methane hydrocarbons, 0.4 nitric oxide and 3.4 carbon monoxide.

At the same time that emissions per kilometre...
have been decreasing in many areas, the amount of driving has continued to increase. The world vehicle population has in fact been growing faster than the overall population; over the last decade, the per capita car population has increased in every corner of the world. Even in the U.S.A., which already had a much greater per capita vehicle population by far than any other area of the world, it continues to increase. In percentage terms, for the world as a whole, cars per capita increased by over 20 per cent during the last decade.

Where Do We Go from Here?

Regional Trends in the Vehicle Fleet

After consideration of the underlying factors influencing vehicle growth, especially population growth and economic development, projections of future vehicle numbers have been made. Estimates of cars, trucks and buses, and motorcycles for the next forty years are given in Figure 2. In making these estimates it was assumed that vehicle saturation, increased congestion and further policy interventions by governments would restrain future growth, especially in highly industrialised areas. In spite of this, vehicles per capita are estimated to continue to rise in all areas of the world. It should be emphasised that without policy interventions, the growth will likely be much higher.

As noted earlier, the global vehicle fleet has tended to be dominated by the highly industrialised areas of North America and Western Europe. This pattern is gradually changing, not because these areas have stopped growing but because growth rates are accelerating in other regions. Early in the next century, based on current trends, the rapidly developing areas of the world, especially Asia, Eastern Europe and Latin America, and the OECD Pacific region will have as many vehicles as North America and Western Europe. Forty years on, North America and OECD Europe could represent less than half the global fleet.

Emissions Rates

The emissions rates for carbon monoxide, hydrocarbons and nitrogen oxides have been estimated, based on exhaust and evaporative emissions standards, fuel quality, maintenance practices, refuelling controls, and Inspection and Maintenance programme status and plans in each country in each of the regions. For countries with no, or very few, pollution control strategies at present it is estimated that they will generally adopt the same programmes as the more environmentally advanced rapidly industrialising countries after a delay of approximately ten years.

Emissions Trends by Region

Projections of future emissions from vehicles around the world are summarised in Figure 3 for each region of the world. Based on a continuation of the strong motor vehicle control programmes in the U.S.A. and Japan, and the recent tightening of requirements in the countries of the European Community, these estimates indicate that global carbon monoxide, hydrocarbons and nitrogen oxides emissions will remain fairly stable throughout the next
decade. Beyond that point, however, emissions of all three pollutants will start to increase due to the projected continued growth in vehicle numbers both in OECD countries and especially in other areas of the world where emissions controls are frequently minimal. This upturn in hydrocarbon and nitrogen oxides emissions will occur shortly after the turn of the century; for carbon monoxide, the downward trend is expected until 2020 when it will also turn up.

Emissions Trends by Vehicle Type

An analysis of the trends in global emissions of carbon monoxide, hydrocarbons, and nitrogen oxides by vehicle type provides some startling insights, as illustrated in Figure 4. First of all, and not surprisingly, cars remain the dominant source of carbon monoxide for the foreseeable future. However, motorcycles, most of which have two-stroke engines, are seen to be significant contributors to hydrocarbons emissions around the world, a fact which is largely ignored in the West due to the small contribution made by motorcycles to pollution in that region. With regard to nitrogen oxides emissions, heavy duty trucks make a large and rapidly growing contribution, due to the minimal nitrogen oxides control of these vehicles in most regions of the world.

Alternative Futures

The Technological State-of-the-Art

Continued growth in emissions from the transportation sector is not inevitable. Even relatively modest steps can significantly lower emissions in the near term, and combined with slight reductions in future vehicle growth patterns, overall stability in emissions from the transport sector is possible.

In the state-of-the-art case, emissions were estimated as if all vehicles in the world were to
Fig. 4 Global trends in carbon monoxide, hydrocarbon and nitrogen oxides emissions from various vehicles show base case projections. Cars will continue to be the major source of carbon monoxide; two-stroke motorcycles will contribute a significant amount of hydrocarbon; heavy duty trucks emit a large and growing amount of nitrogen oxides.

The State-of-the-Art Plus Lower Growth

An additional scenario was analysed which in addition to the more widespread application of the state-of-the-art controls includes lower growth rates in vehicle miles travelled. Under these projections, as illustrated in Figure 5, the vehicle population increases by 30 per cent between 1990 and 2010, and by another 50 per cent to 1.2 thousand million vehicles by 2030. This reflects the much lower per capita vehicle population in non OECD countries compared to OECD countries, the former are projected to grow at a much faster rate in the future.

Trends in global carbon monoxide, hydrocarbons, and nitrogen oxides emissions are shown in Figure 6, assuming that these lower growth rates occur and that the state-of-the-art technologies described above are implemented. Under this scenario, carbon monoxide, hydrocarbons, and nitrogen oxides emissions are constrained below current levels for the next forty years.

Summary and Conclusions

Air pollution is a widespread problem in many countries. Guidelines for air quality, embedded in law in many nations or recommended by such international bodies as the
World Health Organisation, are frequently exceeded in industrialised and less industrialised nations. Such excesses threaten human health, material and economic well-being, and, perhaps most important, ecological stability.

Motor vehicles are the largest single source of man-made volatile organic compounds, nitrogen oxides, and carbon monoxide in the OECD as well as in many rapidly industrialising countries. Controls which reduce these pollutant emissions from this source to the maximum extent technologically feasible are therefore most effective at reducing ozone concentrations. In addition, motor vehicles are probably also the major source of toxic pollutants, and make a significant contribution to potential climate altering emissions.

These emissions cause or contribute to a wide range of adverse health and environmental effects including eye irritation, cough and chest discomfort, headaches, heart disease, upper respiratory illness, increased asthma attacks and reduced pulmonary function. The most recent studies indicate that these emissions can cause cancer and exacerbate mortality and
morbidity from respiratory disease. In addition, studies indicate that air pollution seriously impairs the growth of certain crops, reduces visibility, and in sensitive aquatic systems such as small lakes and streams can destroy fish and other forms of life, and damage forests.

Whether it be localised urban problems, regional smog or global changes, it is clear that motor vehicles are a dominant source of air pollution.

Technologies such as platinum group metals based closed-loop three-way catalyst systems have been developed which have the potential to substantially reduce vehicle emissions in a cost effective manner. Application of these state-of-the-art technologies can improve vehicle performance and drivability, reduce maintenance and facilitate improved fuel economy. Evaporative controls are also readily available and cost effective. The effectiveness of state-of-the-art emissions controls can be improved by in-use vehicle directed programmes such as inspection and maintenance, recall and warranty.

As a result of platinum group metals based catalysts and other controls introduced to date, carbon monoxide, hydrocarbons and nitrogen oxides levels are substantially below what they would otherwise be.

If today's state-of-the-art emissions controls were introduced on all new vehicles around the world, it would be possible to continue to reduce vehicle emissions of carbon monoxide, hydrocarbons and nitrogen oxides while simultaneously absorbing the expected growth in vehicle numbers, at least until early in the next century.

Advances in the state-of-the-art for vehicle technology are emerging and, coupled with more modest vehicle growth, they can constrain global vehicle emissions if they are widely utilised and effectively implemented.

Looking ahead to the future, it is clear that several challenges remain for platinum group metals based catalyst technology. Particular areas of intense activity include:

1. Preheated or very quick light-off systems which will enable manufacturers to comply with the stringent California low emission vehicles requirements.
2. Diesel flow-through particulate catalysts which can lower particulate and the organics associated with diesel combustion without converting too much sulphur dioxide to sulphate.
3. Lean nitrogen oxides catalysts which would enable technologies with inherent lean operating advantages, such as diesels or two-strokes, to take advantage of these capabilities without increasing nitrogen oxides emissions.

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A Decade of Temperature Measurement
SEVENTH INTERNATIONAL SYMPOSIUM REVIEWED

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Platinum has played a central role in temperature measurement for over 100 years, since the early development of platinum resistance thermometers by Siemens and Callendar, and platinum-rhodium thermocouples by Le Chatelier in the late nineteenth century. Platinum resistance thermometers are widely used industrially to BS 1904 (IEC 751) standards, and laboratory instruments with high purity platinum wires have always been the specified instruments for interpolation in the International Temperature Scale (ITS) for the most important part of the range. Currently, in the ITS–90, various patterns of platinum resistance thermometer are used from the triple point of hydrogen (−259.3467°C) to the freezing point of silver (961.78°C). While platinum-rhodium thermocouples are no longer specified for use in the realisation of the scale, they retain their importance as practical secondary standard instruments at high temperatures.

This Symposium was the seventh in a series which have been held in North America about every 10 years. It was organised and sponsored by the U.S. National Institute of Standards and Technology (NIST), the National Research Council (NRC) of Canada, the American Institute of Physics and the Instrument Society of America (ISA), and it was held in Toronto, Canada, from April 28th to May 1st, as part of the ISA spring meeting. About 500 people attended and some 250 papers were presented.

The opening keynote address, by Professor C. A. Swenson of Iowa State University, reviewed the work and events leading up to the adoption of the ITS–90. The technical sessions which followed included papers on all aspects of thermometry: thermodynamic measurements, fixed points and the ITS–90, radiation thermometry, spectroscopic and fibre-optic techniques, applications in industry, medicine and space, etc. Almost half of the papers were in some way concerned with the performance and application of devices using platinum or platinum group metals. Some of the more significant or interesting are now highlighted.

Platinum Resistance Thermometers

The development of the interpolation equations for platinum resistance thermometers now adopted in the ITS–90 was reviewed by L. Crovini of the Istituto di Metrologia “G. Colonnetti” (IMGC), Italy; other papers were concerned with evaluations of their effectiveness; for example, analysing the differences arising from using different thermometers (known as the non-uniqueness of the scale), and the inconsistencies which may arise consequent on the inclusion of overlapping alternative definitions in the scale. G. F. Strouse (NIST), D. I. Head and R. L. Rusby of the National Physical Laboratory (NPL), U.K., and others demonstrated that these effects are tolerably small, generally less than ±0.0005°C over the temperature range up to 420°C. K. D. Hill and D. J. Woods (NRC) described comparison measurements between standard platinum resistance thermometers in a caesium-filled heat pipe which showed differences of less than ±0.002°C in the range from 520°C to 620°C.

Several papers were concerned with the performance, calibration and use of the high temperature platinum resistance thermometers which are now specified for the range up to the freezing point of silver (961.78°C). These require carefully selected materials for their construction so as not to contaminate the platinum, and are generally of low resistance (0.25 to 2.5 ohm) to reduce the effect of electrical leakage at high temperatures. H. G. Nubbemeyer of the Physikalisch-Technische Bundesanstalt (PTB),
Germany, reported on the development and performance of various high temperature platinum resistance thermometers, the short-term stability at the silver point being about 0.001 to 0.002°C, with a long-term value of about 0.005°C. In a joint paper from NIST and the Mendeleev Institute of Metrology in St. Petersburg, G. F. Strouse, B. W. Mangum, A. I. Pokhodun and N. P. Moiseeva reported the results of an investigation into the stability of high temperature platinum resistance thermometers up to the silver point and, in the case of some Russian thermometers, up to the gold point (1064.18°C). They found that extrapolation of the ITS-90 function beyond the silver point caused errors of only 0.004°C.

A European collaborative paper presented by M. V. Chattle (NPL) described the results obtained when thermometers which had been calibrated at the aluminium and silver freezing points were measured at NPL, and then recalibrated at the originating laboratories. In general, the results obtained using a variety of different types of high temperature platinum resistance thermometers and fixed point cells from different sources, showed agreement to within ±0.005°C and ±0.016°C at the aluminium and silver points, respectively.

In contrast to these experimental investigations, J. V. Nicholas, Department of Scientific and Industrial Research, New Zealand, presented a theoretical model for the thermodynamic behaviour of platinum resistivity.

Industrial platinum resistance thermometry was the subject of more than a dozen papers, ranging from one by M. Arai and H. Sakurai of the National Research Laboratory of Metrology (NRLM), Japan, concerning the development of a more robust platinum resistance thermometer for use up to 1100°C, to one by G. Ruffino, P. Coppa, L. de Santoli, A. Castelli and C. Cornaro of Rome University describing the design, construction and testing of a platinum resistance thermometer for inclusion in a probe for the exploration of the Titan atmosphere. Several authors had written papers concerning the resistance/temperature relationships of industrial platinum resistance thermometers together with stability studies carried out in various temperature ranges. J. J. Connolly of the Commonwealth Scientific and Industrial Research Organisation (CSIRO), Australia, reported on industrial platinum resistance thermometer interpolation procedures which lead to uncertainties as low as ±0.01°C up to 250°C, and ±0.05°C at 500°C.

L. Crovini, A. Actis, G. Coggiola and A. Mangano (IMGC) reported the results of their measurements on 100 ohm industrial platinum resistance thermometers of European manufacture; they found that selected thermometers could provide interpolation to within ±0.02°C in the range up to 630°C. However, thermometers for use at higher temperatures (up to 850°C) were less stable and required an additional term to allow for electrical leakage above 630°C. The results of this work will lead to a proposal for revision of the International Standard Tables for industrial platinum resistance thermometers contained in IEC 751, in order to update them to the ITS-90.

The low temperature characteristics of industrial platinum resistance thermometers were reported in papers by Mao Yuzhu, Lin Peng, Zhang Qinggeng and Yue Yi of the Chinese Academy of Sciences with Yao Quanfa and Zhang Jipei of the Shanghai Institute of Process Automation Instrumentation (SIPAI), and by H. Sakurai (NRLM) and T. Nakajima of the Tokyo Metropolitan Industrial Technology Center. Zhang Jipei and his colleagues also reported the results of an investigation into the characteristics of 35 Chinese industrial platinum resistance thermometers at temperatures up to 850°C.

Noble Metal Thermocouples

A number of papers on platinum-rhodium thermocouples presented the results of measurements made to relate the e.m.f.s of types S, R and B thermocouples to temperatures on the ITS-90. Several of them were collaborative papers involving the national standards laboratories of U.S.A., U.K., Italy, The Netherlands, Japan, Korea, China and Russia. The results were collated and analysed.
in a paper presented by G. W. Burns (NIST) and this will form the basis of a proposal to be made regarding the revision of the International Standard Tables for noble metal thermocouples contained in IEC 584–1, in order to align them with the ITS–90.

R. Holanda (NASA) and K. G. Kreider (NIST) both presented papers describing their work on thin-film platinum-rhodium thermocouples; these look promising at temperatures up to about 1500°C. A paper reporting performance data and an ITS–90 based reference function for gold versus platinum thermocouples was presented by G. W. Burns, G. F. Strouse, B. M. Liu and B. W. Mangum (NIST); these thermocouples show promise as highly reproducible secondary standards in the range from 600°C to 1000°C.

Papers on tungsten-rhenium thermocouples included one by Li Baozhang (SIPAI) and Ma Zhenglin (Kunshan Instrument Material Works) which reviewed the development of manufacturing techniques in China and the application of these thermocouples, which are currently undergoing tests in the steel industry as possible alternatives to platinum-rhodium thermocouples. A paper, by N. S. Cannon and R. C. Knight (Westinghouse Hanford Company, U.S.A.), reviewed calibration techniques for tungsten-rhenium thermocouples, with particular reference to the effects of drift.

**Other Applications**

While platinum resistance thermometers and the platinum-rhodium thermocouples represent the main and indispensable uses of the platinum group metals in temperature measurement, many other notable applications were reported at the Symposium. One of these which has seen considerable development in the last ten years is in the use of resistance thermometers based on an alloy of rhodium with 0.5 per cent iron. Originally these were developed for use at very low temperatures (see *Platinum Metals Rev.*, 1992, 36, (1), 11, and *ibid.*, 1981, 25, (2), 57) and this continues to be their main role. G. Schuster (PTB) described the remarkable precision of measurements below 0.05 K, and W. E. Fogle, J. H. Colwell and R. J. Soulen Jr. (NIST) reported on the excellent stability for which the thermometers are noted. O. Tamura and H. Sakurai (NRLM) described the effects of various annealing treatments and the characteristics of wire-wound and film type thermometers, while Zhang Jipei (SIPAI) presented reference functions for industrial rhodium-iron thermometers over the whole range from 1 K to 500°C.

Other more exotic uses of platinum group metals at low temperatures included nuclear susceptibility measurements in platinum by magnetic resonance (D. Hechtfscher and G. Schuster, PTB), and the use of superconductive transitions in iridium, at about 0.1 K (J. Bremer and M. Durieux, Leiden University). Electronic (Johnson) noise thermometry was reported at high temperatures by L. Crovini, A. Actis and R. Galleano of IMGC, R. L. Shepard, R. M. Carroll, D. D. Falter of Oak Ridge National Laboratory, Tennessee, with T. V. Blalock and M. J. Roberts of the University of Tennessee, and H. Brixy, R. Hecker, J. Oehmen and W. Setiawan of the Institut für Angewandte Werkstoffforschung with K. F. Rittinghaus and E. Zimmermann of the Zentralab für Elektronik, Jülich, using platinum or refractory alloy resistors as the source of the noise. Industrial applications of combined noise and thermocouple sensors are of interest because they allow the thermocouple calibration to be monitored in situ. Absolute measurements of freezing point temperatures are also becoming possible with good accuracy, such as to challenge the primacy of gas thermometers and radiation thermometers.

In summary, the Symposium was an opportunity to review ten years of development in the standards and practice of temperature measurement and to look forward to future prospects in the field. One point which is not in doubt is the continued dependence of temperature measurement on the platinum group metals. The proceedings of the Symposium are expected to be published towards the end of 1992, by the American Institute of Physics.

*Platinum Metals Rev.*, 1992, 36, (3) 137
Intermetallic Compounds for High-Temperature Structural Use

UNIQUE IRIDIUM AND RUTHENIUM COMPOUNDS

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Materials that are strong at progressively higher temperatures are sought for use in aircraft engines, in order that operating temperatures, and thereby efficiency and performance, can be increased. Intermetallic compounds with high melting temperatures have the promise of higher strength and elastic stiffness while hot, but in most cases they suffer from extreme brittleness at room temperature. An extensive experimental search of intermetallics has identified four binary compositions that are tough at ambient temperature; and, curiously, each compound has a platinum group metal as one of its components. They are AlRu, IrNb, RuSc, and RuTa.

It is unlikely that the costs of these compounds will allow practical turbine blades to be made in the near future. Nevertheless, the existence of favourable properties is encouraging, in that, by further alloying of the base structures and compositions, one or more of them might be transmuted into commercial materials which would still depend on ruthenium or iridium for their good properties.

Identifying the Intermetallics for Investigation

Although many physical parameters affect the mechanical properties of a prospective material, if many materials are to be surveyed it is useful to decide on a few meritorious properties, for which data are generally available, in order to choose materials for initial screening. In this instance the candidates are numerous; a search for intermetallic compounds that melt above 1500°C identified nearly 300 such binary compounds (1).

Two basic physical properties were identified to simplify the screening, these being the melting temperature, $T_m$, and the specific gravity, $q$. Because these properties are insensitive to processing variables and the resultant microstructure, and are only slightly altered by minor variation in alloying elements, they are helpful indicators of several vital properties. The melting temperature is by far the most useful structure-insensitive property. First, it specifies the temperature interval over which materials are solid. Second, its magnitude increases with the stiffness of a material, since the elastic moduli correlate strongly with melting temperature (2). In addition, all models of strengthening give values of flow stress that are proportional to elastic constants, which in turn increase with the melting temperature. Fourth, expansion coefficients (which for convenience should be small) vary inversely with melting temperature. Finally the creep rates define a maximum operating temperature that increases with melting temperature. Approximate limits on operating temperatures for single-phase materials are estimated to lie between $T_m/2$ and $2T_m/3$, with $T_m/2$ being more typical (3).

For aerospace application, and in rotating parts, high specific strength, that is strength per unit density, and specific stiffness are important. Thus the specific gravity enters consideration, and materials with high melting point and low specific gravity are needed.

The choices can be clearly identified by displaying the data on graphs which plot specific gravity versus melting point, using different charts for different crystal structures. Figure 1 is particularly relevant, since it includes all four of the compounds of primary interest here (1). It surveys two of the simplest ordered structures, the B2 CsCl-type cubic lattice, with 2 atoms per unit cell, and the LI_0


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AuCu-type tetragonal lattice, which has 4 atoms per unit cell.

The desired combination of properties occurs in the lower right region of such a diagram. Since no compounds lie there, one works from the lower right towards the upper left for the best prospects. Where specific gravity is overpoweringly important, AlTi, AlNi, and AlCo would be early choices. Of these AlTi and AlNi are already the subjects of intensive activity; AlCo is not, however, because it is extremely brittle. RuSc and AlRu are obvious subsequent choices because of their high melting points.

Preliminary Screening Tests
Simple mechanical tests were selected to characterise strength versus temperature, and to assess room-temperature toughness. Extensive microhardness measurements were carried out, the results giving an indication of strength (4). An absurdly simple “chisel toughness” test was devised, which consisted of applying to samples a chisel and two hammers of different weights in sequence, to define a 4-level toughness scale that is qualitative, but reproducible (4). The highest level, chisel toughness 3 (unbreakable by this test), was attained by the four compounds listed earlier, but by no other single-phase binary intermetallic.

In all, 20 crystal structure types, 90 binary compositions, and 130 ternary or higher order alloys have been studied by such tests (5). The elastic constants were determined for most of them by more conventional techniques.

The brittleness of most high-temperature intermetallics is such that at room temperature a compression test will give no measurable plastic strain prior to fracture. The results presented in Figure 2 are strikingly different, showing limited but definite plastic strains for the two Ll0-based alloys and large plastic strains for the two B2-based alloys. These special properties drew attention to these compounds and led to further studies of them and their alloys (6–9).

Tough Alloys
Some characteristic properties of the four tough compounds are listed in the Table (5). Most noteworthy are the high melting point values, which place these compounds as a group in the
top 17 per cent of all the binary intermetallics that have melting points above 1500°C. Except for RuSc, the moduli are also high, in the top 33 per cent of high-temperature intermetallics.

IrNb

Although IrNb is expensive, it is less so than pure iridium, which at present is used in the radioisotopic thermoelectric power sources employed on satellites in orbit. That is one potential application; another, with a much lower probability for use, is for jet engine blades or disks. The latter is only likely to occur if a significant part of the iridium can be replaced without seriously degrading the properties of IrNb. To date, the replacement attempts—12 alloys with cobalt, niobium and nickel—have not been successful (6). Also, oxidation problems exist, so that coatings would be needed (10).

Much of the toughness is suspected to arise from the fine-scale internal structure that is common—twins in some cases (see Figure 3), and alternating IrNb L1₀ and Ir₁₁Nb₄(oP12) orthorhombic lamellae in others (Figure 4).

RuTa

If RuTa can be developed further, and if lighter alloys such as those based on AlRu do not develop adequately, then RuTa-based alloys might be considered as jet engine materials. They have, however, major problems, these being: oxidation (10), which might be counteracted by coating, and high density, which can be disregarded only if these alloys allow engine temperatures to be significantly

<table>
<thead>
<tr>
<th>Compound</th>
<th>AlRu</th>
<th>IrNb</th>
<th>RuSc</th>
<th>RuTa*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Structure type</td>
<td>B2</td>
<td>L1₀</td>
<td>B2</td>
<td>L1₀</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>7.95</td>
<td>15.20</td>
<td>7.40</td>
<td>14.83</td>
</tr>
<tr>
<td>Young's modulus, GPa</td>
<td>267</td>
<td>268</td>
<td>155</td>
<td>250</td>
</tr>
<tr>
<td>Melting temperature, °C</td>
<td>2060</td>
<td>1900</td>
<td>2200</td>
<td>2080</td>
</tr>
<tr>
<td>Microhardness, GPa</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>at 23°C</td>
<td>3.1</td>
<td>6.9</td>
<td>2.9</td>
<td>9.1</td>
</tr>
<tr>
<td>at 1000°C</td>
<td>2.0</td>
<td>4.0</td>
<td>1.5</td>
<td>2.2</td>
</tr>
</tbody>
</table>

*Average of Ru₁₁Ta₂ and Ru₁₁Ta₂

Fig. 3 This transmission electron micrograph shows fine scale twins in IrNb, an L1₀ tetragonal structure. Dislocations can be seen to cross twin boundaries.
increased. Some twenty-two RuTa-based alloys have been tested, and hardness, toughness, and elastic properties reported (7, 9). Of these, nine were in the highest toughness categories, and an additional seven had toughness equal to that of Ti, Al and TiAl (9), two lower melting point alloys that are well on their way to finding applications in engines or in space.

Replacements of a portion of the ruthenium by cobalt or iron could be made while still retaining most of the room temperature toughness; sample compositions are Co₀.₃₉Ru₀.₃₀Ta₀.₃₀ and Fe₁.₁₃Ru₀.₂₃Ta₀.₅₇. Elastic moduli are decreased by changing the ruthenium content away from 50 atomic per cent, as shown in Figure 5. Single-phase alloys follow the lines drawn while two-phase alloys have considerable scatter.

RuTa, like the other Li₁₀ crystal type IrNb, has a fine structure of twins (Figure 6) or alternating lamellar phases (in this case Li₁₀ and B2) (7). As Figure 7 shows, the layer structure appears clearly on fracture surfaces. Plasticity and toughness are thought to be strongly affected.

AlRu (and RuSc)

For aerospace applications the B2 compounds appear to be more promising than those with the Li₁₀ structure because of their greater ductility and lower specific gravities; and AlRu suffers the least from oxidation. The data imply that uncoated Al₀.₄₅Ru₀.₅₅ and Al₀.₄₅Ru₀.₅₅Y could

![Platinum Metals Rev., 1992, 36, (3)](141)
be used at temperatures up to $1250^\circ C$ (10). Scandium makes pure RuSc unusually expensive, but the fact that RuSc has good mechanical properties has been used to infer, rightly, that additions of scandium, replacing some of the aluminium in AlRu might result in improved properties (8, 9).

Many AlRu-based materials have been tested. Among several dozen compositions, twenty-one were designed to test solid solution hardening by cobalt, iron, and titanium, twenty-two were used to explore off-stoichiometry effects and the effects of boron and scandium on toughness and strength, and eight were concerned with the effects of adding a variety of elements (cerium, chromium, rhenium, silicon and yttrium) which were intended to lower oxidation rates.

The ruthenium concentration had a powerful effect on the elastic properties of RuTa in the composition range of 43–60 atomic per cent; here Young’s modulus was raised by about 1 per cent for each per cent increase in ruthenium content. Among the other alloying additions only scandium exerted a significant effect, which was of lowering the moduli by about 1 per cent for each percentage addition.

Stoichiometry and minor additions of boron have profound influences on the plasticity of AlRu-based materials, as Figure 8 shows. Compounds that are sub-stoichiometric in ruthenium are brittle at grain boundaries, but the plasticity of AlRu is clear, and both work hardening and strain-to-fracture increase with the fraction of ruthenium. Also apparent is the beneficial effect of adding 0.5 per cent of boron, which doubled the plastic strain and maximum stress. The boron is also effective at that level for sub-stoichiometric and stoichiometric alloys. Figure 9 shows this behaviour, and also that the particular concentration of 0.5 per cent boron was a happy choice, since both lesser and greater levels were ineffective.

The scanning electron micrographs of fracture surfaces presented in Figure 10 show the...
Fig. 8 Compressive stress-strain tests of Al-Ru alloys at 23°C show extensive plasticity and high work hardening which increases with the ruthenium concentration.

Fig. 9 There is a peak at 0.5 atomic per cent in the maximum strain in compression of Al-Ru alloys as a function of the boron content and of Al:Ru ratios. Al$_{33}$Ru$_{47}$ alloys are intergranularly brittle and are enriched in aluminium at the grain boundaries.

striking change in surface character that results from increasing the ruthenium content from 47 to 53 per cent and from adding 0.5 per cent boron. Al$_{33}$Ru$_{47}$ is intergranularly brittle; Al$_{33}$Ru$_{47}$ + 0.5 per cent boron is tough, with a fibrous fracture surface. The intergranular
brittleness and its cure by boron addition is reminiscent of the situation in $\text{Ni}_3\text{Al}$ (11), the base material for nickel-based superalloys, which are the present materials of choice for jet engine blades and disks.

Scandium was thought to be a possible solid solution substitution for aluminium since $\text{RuSc}$ and $\text{AlRu}$ have in common the $\text{B}2(c\text{P}2)\text{CsCl}$ structure (12), and since their lattice constants ($3.1985 \pm 0.0006 \text{ Å}$ and $2.9916 \pm 0.0007 \text{ Å}$, respectively) differ by only 6.9 per cent. Nevertheless, even minor scandium additions led to the appearance of a second phase (8), but one with helpful effects on the high-temperature strengths as inferred from microhardness measurements. However, 10 per cent scandium or more greatly decreased the toughness (8), but the use of boron to improve ductility and toughness was again successful for compositions with lower scandium content. Figure 11 compares the hardness of stoichiometric $\text{AlRu}$ with that of two alloys, one containing 5 per cent scandium and the other 4 per cent scandium and 0.5 per cent boron. Both have improved hardness to 1150°C, and the boron-containing alloy has outstanding toughness. Another alloy with 2 per cent scandium and 1.5 per cent boron was nearly as tough.

Ternary Alloys

Recently both toughness and tensile ductility have been found by Waterstrat, Bendersky and Kuentzler in a ternary $\text{B}2(c\text{P}2)$ structure, $\text{Zr(Pd}_0.5\text{Ru}_0.5)$, which contains two platinum group metals (13). Although cracks formed at about 1 per cent tensile strain, macroscopic fracture occurred at greater than 6 per cent strain. Slip with $<100>$ slip vectors was accompanied by the additional deformation mode of $\{114\}$ twinning, which was suggested to be the mechanism that allowed plasticity. The melting point is bracketed in the range as 1800 ± 200°C.

Overview and Potential Uses

As noted in the second paragraph of this article, cost is one major obstacle in the use of ruthenium-based materials in jet engine components. In part, costs might be reduced in the future by partially replacing ruthenium with lighter, less expensive elements. Prices may decrease if more massive demand leads to reduced costs of production or to discoveries of new ore. Improvements in advanced jet engines are driven by military demands, which are much less governed by cost than are commercial customers. Therefore, military engines are the first candidates for engine applications. A final critical obstacle to use is that although the preliminary properties are encouraging, many rigorous tests still need to be passed before it is clear whether these materials are technically capable of being used in engines. As R. Sprague of the General Electric Company has noted, "The first thing you ever hear about a new material is usually the best thing you ever hear."

The possible use of $\text{IrNb}$ alloys in place of iridium in radioisotopic thermoelectric generators is an even more specialised application, and it remains speculative. $\text{Zr(Pd}_0.7\text{Ru}_0.3)$ is being evaluated as a dental alloy, where cost is a minor consideration.

In a personal communication Dr. M. B. Cor-tie has noted that ruthenium commonly aids corrosion resistance, and that $\text{AlRu}$-based alloys may therefore be useful in applications where corrosion resistance at unusually high temperatures is vital.
Platinum Utilisation in Fuel Cell Electrodes

Due to its ability to provide much higher power densities, the proton exchange membrane fuel cell is the leading fuel cell contender for power generation in both vehicular and stationary applications in the 5–500 kW range. The proton exchange membrane cell operates below 100°C and uses a solid film of immobilised fluorocarbon ion-exchange membrane as electrolyte. This provides a more rugged unit and faster start-up from room temperature than other types of fuel cell. Recent Californian State regulations calling for 2 per cent of all new vehicles to be zem emitting by 1998, the percentage increasing to 10 by 2003, has renewed interest in the development of this clean and efficient power generation system.

A Commercialisation Requirement

One of the major impediments to the wider commercialisation of currently available proton exchange membrane fuel cell technology is the high platinum content of the electrocatalyst used to catalyse the hydrogen oxidation and oxygen reduction reactions. With loadings of around 4.0 mg Pt/cm² on each electrode, the platinum cost is over $300/kW. To achieve commercial success catalyst costs may have to be reduced by a factor of around 50, while maintaining the high power outputs.

In conventional fuel cells, relying on the diffusion of the liquid electrolyte into the electrode, it is possible to utilise nearly all the platinum catalyst in the porous electrode to catalyse the electrochemical reactions. Proton exchange membrane cells make use of a solid polymer electrolyte and up to now high platinum utilisation has been difficult to achieve; hence the current prohibitively high loadings of platinum catalyst required.

Two recent publications, one from the Los Alamos National Laboratory (M. S. Wilson and S. Gottesfeld, *J. Electrochem. Soc.*, 1992, 139, (2), L28–30) and the other from Physical Sciences Incorporated, of Massachusetts (E. J. Taylor, E. B. Anderson and N. R. K. Vilambi, *J. Electrochem. Soc.*, 1992, 139, (5), L45–46), describe the preparation of new, extremely low platinum loading, high performance proton exchange membrane fuel cell electrodes. The Los Alamos group describe a new “thin film catalyst” in which catalyst layers are cast directly onto the solid electrolyte membrane from inks consisting of carbon supported platinum catalyst mixed with a solubilised form of Du Pont’s Nafion ion-exchange membrane. During tests, electrode assemblies with platinum loadings of 0.13 mg/cm² gave 2 A/cm² at 0.6 V, which is comparable with current state-of-the-art technology. The approach adopted by Physical Sciences Inc. involves preparing a gas diffusion electrode from uncatalysed carbon into which the soluble form of Nafion is impregnated. Finely dispersed platinum particles are then electrodeposited from a commercial platinum plating bath, apparently only into regions of the electrode having both ionic and electronic conductivity. Electrodes containing 0.05 mg Pt/cm² generated currents which again are comparable with state-of-the-art technology.

The high performance of these new electrodes with such remarkably low levels of platinum is attributed to better utilisation of the platinum. If these laboratory performances can be realised when scaled-up into practical fuel cell stack systems, they may indeed provide a major breakthrough in the advancement to commercialisation of the proton exchange membrane fuel cell system. At the very least they amply demonstrate the technical feasibility of achieving significant platinum cost reductions.

G.A.H.

References


*Platinum Metals Rev.*, 1992, 36, (3) 145
Refining Secondary Iridium by an Oxidative Method

By A. V. Yermakov, V. M. Koltygin and E. V. Fatyushina
Laboratory of Strength, Ural State University, Ekaterinburg, Russia

The majority of investigators reporting on the mechanical properties of iridium have noted its high sensitivity to impurities. The elements which may have caused embrittlement are carbon, oxygen, and the refractory metals tungsten and rhenium. The segregation of these impurities to the grain boundaries in pure iridium has been considered to be the cause of brittleness in samples which failed after less than 5 per cent elongation at room temperature (1). The reduction in metallic impurities, and in carbon and oxygen, to a level of parts per million, allows iridium to be successfully used at temperatures of 1100 K and higher (2).

Iridium crucibles are subjected to repeated thermal cycles for long periods of time at high temperatures. These large iridium crucibles are used to grow single crystals of gallium-gadolinium-garnet and aluminium-yttrium-garnet. The resulting scrap material may be contaminated with platinum, palladium, rhodium, iron, tungsten, molybdenum, magnesium, nickel, silicon, calcium, copper, oxygen, carbon and oxides of aluminium, yttrium, gadolinium, gallium and zirconium. The scrap is likely to contain 95 to 98 weight per cent iridium. The conventional method of producing high purity iridium by chemical refining is extremely labour intensive, and results in significant loss of the metal (3).

A number of alternative methods of purification are known, and one of them is considered here. This process involves oxidation of the impurities during air melting of the scrap iridium in a periclase crucible (periclase contains, in weight per cent, 96 MgO, 1 Al₂O₃, 1.2 CaO, 1 Fe₂O₃ and 0.8 SiO₂). During this process the iridium exhibits extreme inactivity at the high temperatures used, 2715 to 3000 K (4). The reactions of the contaminating materials can be classified into two groups according to their characteristic interactions with oxygen in the air at the melting point of iridium, and at even higher temperatures:
1. Elements which form stable oxides: aluminium, yttrium, gadolinium, gallium, iron, tungsten, carbon, molybdenum, niobium, magnesium, silicon and zirconium.
2. Elements having oxides which dissociate below the melting temperature of iridium, namely: platinum, palladium, rhodium, nickel and copper.

Calculation of the Concentration Equilibrium of Impurity Elements

The possibility of removing the first group of elements from iridium was calculated from the Free Energy of these elements at 3000 K and pressure of 10⁷ Pa, and from the resultant equilibrium concentrations of the impurities and the stable oxides. The equilibrium concentrations of the oxides of these elements with liquid iridium was determined from the equilibrium concentration of the impurities, and the final analysis of the liquid iridium. Melting the iridium in a periclase crucible formed a slag based on periclase which allowed better removal of most of the impurities. The calculations were performed on systems consisting of “iridium with impurities-oxygen in air”, at temperatures of 2800 to 3000 K, approaching those of the ideal solutions (5). During the calculations, consideration was given to the condensation of the metal and slag phases and also to the migration, in the gas phase, of volatile oxides which have high partial pressures. Atomic adsorption analysis data show that concentrations of oxide impurities in the slag, which did not enter the periclase, were not more than 0.1 weight per cent. Partial
Calculated and Experimental Data of the Impurity Concentrations of Elements in Iridium Scrap after Induction-Oxidation Melting

<table>
<thead>
<tr>
<th>Element</th>
<th>Initial concentration, at. %</th>
<th>Partial pressure of oxides at 3000 K, $\times 10^2$ Pa</th>
<th>Equilibrium concentration of impurities in liquid iridium, at. %, in systems</th>
<th>Experimental contents of impurities, at. %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Iridium-Air</td>
<td>Iridium-Argon</td>
<td></td>
</tr>
<tr>
<td>Al*</td>
<td>0.2</td>
<td>0.813</td>
<td>$1.6 \times 10^{-3}$</td>
<td>$4 \times 10^{-4}$</td>
</tr>
<tr>
<td>Y*</td>
<td>0.05</td>
<td>1.093</td>
<td>$4.3 \times 10^{-5}$</td>
<td>n.r.</td>
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<tr>
<td>Gd</td>
<td>0.15</td>
<td>0.533</td>
<td>$2.9 \times 10^{-5}$</td>
<td>$2.6 \times 10^{-8}$</td>
</tr>
<tr>
<td>Zr*</td>
<td>0.05</td>
<td>0.187</td>
<td>$2.6 \times 10^{-5}$</td>
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<tr>
<td>Si</td>
<td>0.01</td>
<td>289.3</td>
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<td>$8.9 \times 10^{-4}$</td>
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<tr>
<td>Nb</td>
<td>0.05</td>
<td>19.5</td>
<td>$1.7 \times 10^{-3}$</td>
<td>$1.9 \times 10^{-5}$</td>
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<tr>
<td>Fe</td>
<td>0.8</td>
<td>169.3</td>
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</tr>
<tr>
<td>Ca</td>
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<td>n.r.</td>
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<td>W</td>
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<td>Mo</td>
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<td>Ga*</td>
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<td>C</td>
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<td>O</td>
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<tr>
<td>Cu</td>
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<tr>
<td>Ni</td>
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<tr>
<td>Pd</td>
<td>0.01</td>
<td>48</td>
<td>$2.3 \times 10^{-2}$</td>
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</tr>
<tr>
<td>Mg</td>
<td>0.01</td>
<td>48</td>
<td>$2.7 \times 10^{-1}$</td>
<td>$7 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

* Al, Y, Gd, Zr: additive elements found in charge as oxides
n.u. — impurities could not be removed
n.r. — contents of elements were not determined
n.o. — equilibrium contents of additives were not calculated

pressures of gas forming oxides in the given temperature range have been studied previously (6). Calculated values of the maximum equilibrium concentrations of the impurities in iridium after induction-oxidation melting are given in the Table.

In addition, iridium purification could occur by evaporation of some impurities from the melt. These processes are limited by the fact that melting takes place at atmospheric pressure, but contaminants from both groups with high partial vapour pressures were removed from the iridium.

In previous work the systems “iridium with impurities-inert gas (argon)” were studied at temperatures of 2000 to 4000 K and at pressures of $9.8 \times 10^{-2}$ to $1.3 \times 10^{-8}$ MPa, and the evaporation of elements such as platinum, rhodium, aluminium, magnesium, tungsten, iron, nickel, copper, silicon, zirconium and carbon were described (7). Calculations were performed on the basis of the “maximum entropy” principle: entropies of the gaseous phase and of the components in the condensed state. The low concentrations of impurities allow calculation of ideal solutions. The results of the calculations are given in the above Table.

**Experimental Studies of Impurity Behaviour**

In order to compare theoretical and experimental data, a series of oxidation-induction melting experiments were performed on iridium scrap containing the impurities listed in the Table. Melting was carried out in air using a periclase crucible with porosity of less than 4 to 5 per cent. The iridium was maintained in

*Platinum Metals Rev.*, 1992, 36, (3)
the liquid state for a period of 30 minutes, at a temperature of around 3000 K. Before the metal was cooled in the crucible, 20 to 30 g samples of molten iridium were taken for control measurements. The compositions of the impurities were established by mass spectroscopy. The selected regimes allowed measurements to be made of impurities present in the iridium at concentrations of the order of $10^{-7} - 10^{-8}$ atomic per cent. The experimental data are also presented in the Table.

The experimental concentration values for aluminium, yttrium, gadolinium, zirconium, silicon, iron, molybdenum, gallium, copper, nickel, palladium and magnesium, agree well with the calculated data. On the basis of these results, it is possible to conclude that iridium refining can be carried out by the following methods:

1. The oxidation of impurities which form stable oxides during the induction-oxidation melting process. These, together with the oxides in the furnace charge, then enter into the slag. The removal of aluminium, yttrium, gadolinium, zirconium, silicon, niobium, iron and calcium from the iridium was carried out by this method.

2. The formation of oxides of the contaminants which have high partial pressure, such as tungsten, molybdenum, gallium, carbon, and which evaporated during melting.

3. The removal of impurities such as copper, nickel, palladium and magnesium which occurred due to evaporation because they have higher partial pressures than iridium.

For calcium and niobium, the level of purity obtained was higher than that calculated. This may be due to the formation of chemically stable oxides with MgO, resulting in a sharp fall in CaO and NbO activities in the slag and a decrease of calcium and niobium concentrations in the melt. The final concentration of tungsten was higher than the calculated value. This result shows that tungsten removal is dependent on the kinetics of the reaction for its removal from the melt. When air was introduced into the iridium melt the tungsten formed a volatile oxide and its removal was increased (8).

**Discussion of the Results**

The agreement of the calculated data with figures obtained experimentally showed that the method of calculation used, and the assumptions made, were correct. Effective removal of contaminants from iridium results from better contact of the melt with the periclase crucible, thus binding part of the oxides, and intensive mixing of the melt with the help of an electromagnetic field. However, during induction-oxidation melting platinum and rhodium, which have properties similar to those of iridium, were not removed from the iridium. Also only a partial reduction in the concentration of the impurities of iron, gallium, palladium, oxygen, copper and nickel occurred. These elements can be removed more effectively from iridium by electron-beam melting, after which the concentrations of platinum and rhodium decrease to $10^{-3} - 10^{-4}$ atomic per cent, and residual impurities to $10^{-4} - 10^{-5}$ atomic per cent. The metal impurities which are removed in this way from
iridium scrap have been picked-up during single crystal growth in crucibles and from iron-based apparatus used during the formation of these large crucibles.

After induction-oxidation melting iridium can be worked. The results of compression studies carried out at room temperature are given in Figure 1.

Samples cut from a coarse grained ingot produced by induction melting were also investigated. This material was cold worked into single crystals that were found to be strong, which may be due in some way to the increased concentration of elements such as oxygen and iron in the iridium.

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Protecting Tantalum by Platinum Implantation

Tantalum is a suitable material for use in corrosive environments, due to the formation of a dense highly resistant oxide film on its surface. In hot concentrated mineral acids, however, it is attacked and although the loss of material may be acceptable in some circumstances the associated electrochemical evolution of hydrogen can cause serious problems. Tantalum readily forms hydrides, which are brittle and therefore cause loss of mechanical strength which could, perhaps, result in component failure.

It is known that palladium and platinum can protect tantalum from embrittlement, it is also known that a titanium surface modified by ion implantation with an electrocatalytically active metal can be effective in reducing corrosion. Now a communication from the University of Heidelberg, Germany, reports the results of an investigation of tantalum following platinum ion implantation, and its effect on hydrogen embrittlement ("Electrocatalytic Protection against Hydrogen Embrittlement of Tantalum in Strong Acids by Platinum Ion Implantation", W. Ensinger and G. K. Wolf, *Surf. Coat. Technol.*, 1992, 51, (1–3), 41–44).

Even a very small amount of platinum implanted in the surface of tantalum has a significant influence on the embrittlement by hydrogen, as determined by a mechanical bend test. Both the amount of platinum implanted, and the rate at which it was implanted had an effect on sample life; a low charging current and a high implantation dose being the most effective conditions. Implanted platinum reduces hydrogen adsorption electrochemically, it also decreases the entire corrosion process, including the cathodic hydrogen evolution reaction, and is effective for a long time in extremely corrosive environments, even though only a shallow layer of tantalum is modified. Thus tantalum implanted with platinum has greater scope as a constructional or protective material.

The Chemistry of the Platinum Group Metals

The fifth International Conference on the Chemistry of the Platinum Group Metals will be held at the University of St. Andrews, Scotland, from 11th to 16th July, 1993. The conference will be organised by the Dalton Division of the Royal Society of Chemistry and provides an important opportunity for researchers in the field to meet and discuss recent developments.

Topics to be covered include applications of platinum group metals in organic synthesis, materials science, biology and medicine; their electrochemistry; advances in homogeneous catalysis, co-ordination chemistry, clusters, particles and the solid state.

People wishing to contribute or to receive further information should contact Dr. John F. Gibson, Secretary (Scientific), Royal Society of Chemistry, Burlington House, Piccadilly, London W1V 0BN, England.
Platinum 1992

PLATINUM SUPPLY AND DEMAND REACHED RECORD LEVELS

The eighth annual survey of the platinum group metals was published by Johnson Matthey in May and is based, for the most part, on information available up to the end of March 1992. During 1991 both the supply and demand for platinum were the highest ever, at 4.16 and 4.04 million ounces, respectively, the former being boosted by Russian sales. This increase in supply was only one of several factors that contributed to a lowering of prices, the average London fixing being U.S. $376 in 1991 compared with U.S. $472 in 1990.

Once again the largest application for platinum was for automobile catalysts, as an increasing number of cars in Europe were fitted with catalytic converters, and as emissions standards were introduced in additional countries. Demand amounted to some 1.57 million ounces. This was closely followed by demand from the jewellery sector, at 1.47 million ounces worldwide, over 85 per cent of which was taken by Japan. Usage in the chemical industry fluctuated with changes in the various components that make up this sector. The use of platinum in connection with motor vehicles is not restricted to its use in catalytic converters, which are featured in a separate section of the report, as petroleum refining is already an established application for platinum catalysts. Now platinum is also used in a new process to catalyse the production of iso-butylene, a feed material for methyl tertiary butyl ether which is added to gasoline as an octane improver. Furthermore, the electronic management systems that are required to optimise vehicle fuel injection and enable autocatalysts to function effectively depend upon platinum sensors. Although the quantity of platinum in each sensor is very small, the total requirement is significant. Increasingly spark plugs are also incorporating platinum tips to increase engine efficiency and reduce pollutant emissions.

The average price for palladium was U.S. $88, down U.S. $27 from 1990 prices as supplies outstripped demand for the second successive year. 1.82 million ounces, approximately fifty per cent of demand, were used in electronic components. While the use of hybrid integrated circuits containing silver-palladium conductive tracks has declined, the production of multi-layer ceramic capacitors, which generally use pure palladium or silver-palladium as the conductive material, has increased. The demand for palladium for dental alloys rose from the 1990 figure of 1.02 million ounces to 1.07 million ounces.

Both the supply and demand for rhodium were lower than in 1990. Its outstanding activity for nitrogen oxides reduction, coupled with its ability to convert the other major pollutants in exhaust emissions, ensures its presence in three-way catalysts and explains why over 80 per cent of consumption was by the automobile industry.

In 1991 demand for ruthenium rose to 169,000 ounces, with some 64 per cent being used in the electrical sector as a resistive material. The chemical industry accounted for 34 per cent of demand; the use of ruthenium coated titanium anodes for the electrolysis of brine is slowly decreasing as the pulp and paper industry replaces chlorine with sodium chlorate and hydrogen peroxide, now regarded as "environmentally friendly" bleaching agents. Production of these utilises iridium-platinum electrodes and palladium catalysts, respectively.

Readers of Platinum Metals Review who do not have ready access to this important fifty-six page survey of the commercial aspects of the platinum group metals, and who require an authoritative source of such information, are invited to address their requests to the author: Mr. Jeremy S. Coombes, Johnson Matthey P.L.C., New Garden House, 78 Hatton Garden, London ECIN 8JP, England; Fax 071-269 8135.
The Structure of Platinum-Tin Reforming Catalysts

By R. Srinivasan and Burtron H. Davis
Center for Applied Energy Research, University of Kentucky, Lexington, U.S.A.

Platinum-tin on alumina catalysts appear to have potential for use during naphtha reforming in processes utilising continuous catalyst regeneration, and without the need for complex activation procedures. To gain a better understanding of the properties that contribute to their effectiveness, the surface and bulk characteristics of these bimetallic catalysts have been studied by a variety of techniques which make more direct measures of the chemical and physical states of the elements present than, for example, temperature-programmed reduction. The data presented demonstrate that catalyst formation by the addition of platinum and tin by co-precipitation leads to alloy formation, but that this does not occur when a support prepared by co-precipitating tin and aluminium oxide is impregnated with chloroplatinic acid.

The introduction of the bifunctional platinum/alumina catalyst for naphtha reforming shortly after the end of World War II led to a revolution in petroleum processing (1). On the commercial side, the reforming process provided a means of meeting the dramatic increase required in octane rating for gasoline, to provide an abundant source of aromatics for the rapidly developing petrochemicals industry, and to provide surplus hydrogen and so permit the development of other processes such as hydrocracking. On the scientific side, the studies needed to define the mechanisms underlying the effectiveness of this bifunctional catalyst led to significant advances in the understanding of catalysis as well as of the reforming process.

While the platinum/alumina catalysts were an outstanding success, they had to be regenerated at rather frequent intervals: every three months or so. Thus, the introduction in the late 1960s of a platinum-rhenium bimetallic catalyst that could remain on-stream for a period of a year or even longer led to a second revolution in naphtha reforming (2). The platinum-rhenium/alumina catalyst had to be activated and brought on stream using a rather lengthy procedure which usually involved poisoning the catalyst with sulphur during a break-in period. Today, with the potential for a naphtha reforming process incorporating continuous catalyst regeneration, other bimetallic catalysts which do not require complex activation procedures must be utilised; platinum-tin/alumina appears to be an attractive catalyst for this process.

The reasons for the superior catalytic properties of these bimetallic catalysts are not fully understood even after 30 years of active research. Many of the explanations for the superior properties of the bimetallic catalysts are based on a structural point of view. Many argue that the bimetallic components form an alloy which has better catalytic properties than platinum alone. For example, alloy formation could influence the d-band electron concentration, thereby controlling selectivity and activity (3). On the other hand, the superior activity and selectivity may be the result of high dispersion of the active platinum component, and the stabilisation of the dispersed phase by the second component (4). Thus, much effort has been expended in order to define the extent to which metallic alloys are formed (for example, see References 5–18). These studies have
Platinum and tin present a complex situation since a number of alloy compositions are possible, depending upon the tin to platinum ratio. The phase diagram in Figure 1 shows that as the tin to platinum ratio increases it should be possible to form a series of alloys with increasing tin fractions (19, 20).

Temperature-programmed reduction (TPR), one of the indirect analysis methods, yielded data which suggested that tin was not reduced to the zero-valent state (10, 16). Burch has reviewed early work on the characterisation of this type of catalyst in an earlier issue of this journal (15). Based on results obtained from TPR studies, Lieske and Volter reported that a portion of the tin in platinum-tin/alumina catalysts was present in the zero valence state (23); furthermore, it appears that the atomic ratio of the platinum-tin alloy, based upon the amount of platinum and tin(0) detected by XPS, increases with increasing ratios of tin to platinum. Typical spectra for the tin 3d_{3/2}, 3d_{5/2} regions of a reduced catalyst having a platinum:tin composition of 1:8 (all catalysts contained 1 weight per cent platinum) are shown in Figure 2 (24). The spectrum for platinum in Figure 3 has been corrected for sample charging by using an aluminium 2p peak position of 74.7 eV. A small peak at approximately 480 eV is due to a small amount of tin that is present on the palladium sample holder. This small peak and the palladium peaks of the sample holder do not experience charging; this small tin peak is at a position indicative of metallic tin (or tin oxide in the oxidised sample) prior to correction for charging.

The spectra for the aluminium 2p and the platinum 4f regions are shown in Figure 3 for the same platinum to tin ratio of 1:8 sample. Because the aluminium 2p peak of the alumina support overlaps with the platinum 4f peaks, curve deconvolution was carefully carried out assuming the intensity ratio of 4f_{5/2} to 4f_{7/2}. studies allow determination of the chemical state of an element but the data do not permit one to define whether tin(0), if present, is in the form of a platinum-tin alloy. Furthermore, the major platinum XPS peak coincides with a large peak from the alumina support. Thus, XPS can only provide data to indicate whether an alloy is possible; it cannot be used to prove the presence of a platinum-tin alloy.

The early XPS studies, including those from our laboratory, revealed that the tin is present only in an oxidised state (10, 16). These results were consistent with those for platinum-rhenium bimetallic catalysts where only oxidised rhenium was observed (9, 22). The early XPS data, at least from our laboratory, were apparently affected by the use of oxygen-containing pump oils to maintain the high vacuum needed for the operation of the XPS instrument. Thus, Li and co-workers reported that a portion of the tin in platinum-tin/alumina catalysts was present in the zero valence state (23); furthermore, it appears that the atomic ratio of the platinum-tin alloy, based upon the amount of platinum and tin(0) detected by XPS, increases with increasing ratios of tin to platinum. Typical spectra for the tin 3d_{3/2}, 3d_{5/2} regions of a reduced catalyst having a platinum:tin composition of 1:8 (all catalysts contained 1 weight per cent platinum) are shown in Figure 2 (24). The spectrum for platinum in Figure 3 has been corrected for sample charging by using an aluminium 2p peak position of 74.7 eV. A small peak at approximately 480 eV is due to a small amount of tin that is present on the palladium sample holder. This small peak and the palladium peaks of the sample holder do not experience charging; this small tin peak is at a position indicative of metallic tin (or tin oxide in the oxidised sample) prior to correction for charging.

In the following text, we report data from methods which make a more direct measure of the chemical or physical state of the platinum and/or tin present in platinum-tin/alumina catalysts; but because of space limitations this review outlines results primarily from our laboratory.

X-ray photoelectron spectroscopy (XPS)
was 0.75:1.0. The binding energies of the platinum peaks in Figure 3 are consistent with platinum being present as platinum(0). In this study three catalyst series were analysed using XPS. The compositions of the platinum-tin alloys (calculated by assuming all the platinum and the fraction of tin present as tin(0) formed an alloy) that are present in each catalyst of the three series are summarised in Table I. It appears that the alloy present contains increasing platinum:tin ratios as the ratio of platinum to tin on the catalyst is increased. However, XPS provides a measure of the surface, and not the bulk, composition; Bouwman and Biloen showed that tin is concentrated in the surface of a reduced sample of unsupported platinum-tin alloy (25). Our XPS results are in general agreement with those obtained in the extensive investigations by Hoflund and co-workers (26–32).

Stencial and co-workers utilised XPS together with scanning electron microscopy (SEM) to follow the interaction and migration of chlorine in platinum, rhodium and platinum-tin-containing catalysts (33). In situ reduction with hydrogen decreased the surface concentration of chloride, presumably by increasing the bulk chloride concentration. Subsequent oxygen treatment of these reduced catalysts caused the surface concentration of chloride to increase. In the case of rhodium/alumina, the characteristics of the aluminium 2p peak after
hydrogen reduction suggest the formation of AlCl₃-type species.

¹¹⁹Sn Mössbauer data also provide a bulk diagnostic technique which has been utilised in a number of studies (for example, 7, 34–47). Direct evidence for platinum-tin alloy formation was obtained from Mössbauer studies (for example, 7, 42, 43, 46, 47); however, many of these studies were at high metal loadings and even then such a complex spectrum was obtained that there was some uncertainty in assigning tin(0) to the exclusion of tin oxide phases.

<table>
<thead>
<tr>
<th>Pt:Sn Alloy Compositions Based upon XPS Data</th>
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<tbody>
<tr>
<td>Support</td>
</tr>
<tr>
<td>-------------------------------------------</td>
</tr>
<tr>
<td>Pt:Sn</td>
</tr>
<tr>
<td>Alumina, 250 m²/g</td>
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<tr>
<td>Alumina, 110 m²/g</td>
</tr>
<tr>
<td>Silica</td>
</tr>
<tr>
<td>1:1</td>
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<tr>
<td>PtSn₅₆</td>
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<tr>
<td>PtSn₅₆</td>
</tr>
<tr>
<td>PtSn₁₅</td>
</tr>
<tr>
<td>PtSn₁₅</td>
</tr>
<tr>
<td>1:5</td>
</tr>
<tr>
<td>PtSn₃₄</td>
</tr>
<tr>
<td>PtSn₃₄</td>
</tr>
<tr>
<td>PtSn₂₆</td>
</tr>
<tr>
<td>PtSn₂₆</td>
</tr>
<tr>
<td>1:8</td>
</tr>
</tbody>
</table>

*Platinum Metals Rev.*, 1992, 36, (3)
Mössbauer results clearly show changes upon reduction in hydrogen, but the width of the peaks for the reduced sample prevents, in general, a specific assignment for some states of tin. This is exemplified by the results of Kuznetsov and co-workers, who reported that platinum-tin/γ-alumina catalysts prepared by conventional impregnation techniques are multicomponent (42); that is, they have highly dispersed species that are a result of chemical interactions of tin(IV), tin(II), and tin(0) with both the support surface and the platinum. According to these authors, platinum forms nearly all possible alloys with tin. Examples of Mössbauer spectra and the isomer shifts associated with particular compounds or alloys are presented in Figure 4 (35).

The same series of catalysts that had been used earlier in their XPS studies (23) was utilised by Li and co-workers (48); each sample in the three series contained 1 weight per cent platinum and a varying amount of tin. Tin was observed to be present in forms whose isomer shifts were similar to or the same as those of SnO₂, SnO, SnCl₄, SnCl₂, tin(0) and platinum-tin alloy, when alumina was the support. Representative Mössbauer spectra are shown in Figure 5. If it is assumed that the platinum-tin alloy only has the atomic ratio tin:platinum of 1:1, as was found to be the case in X-ray diffraction (XRD) data to be described below, one obtains the results shown in Figure 6. For lower tin to platinum ratios (< 5) little difference is observed in the extent of alloy formation and the distribution of the oxidised species, for a low and high surface area alumina support. In this respect, there is general agreement with data observed in some of the earlier Mössbauer studies. The Mössbauer data in Figure 6 show a similar trend in the extent of alloy formation for the alumina supported
DIFFRACTION ANGLE.

A catalyst was prepared by impregnating a Degussa Aluminium Oxide C (a non-porous alumina of surface area 110 m²/g) with an acetone solution of [Pt₃Sn₃Cl₁₀]²⁻ (50). A sample of a catalyst containing 5 weight per cent platinum was reduced in situ in the chamber of an XRD instrument; thus the material was not exposed to the atmosphere prior to recording the X-ray diffraction pattern (51). The X-ray diffraction patterns shown in Figure 7 match very well, both in position and intensity, the pattern reported for platinum-tin alloy (Figure 8). In Figure 8, it can be seen that with the 5 weight per cent platinum catalyst, a small fraction of the platinum is present as crystalline platinum but that crystalline platinum was not observed for the 0.6 weight per cent platinum catalyst. It is noted that a similar result for the platinum-tin alloy is obtained for a catalyst that contains only 0.6 weight per cent platinum, with the same tin to platinum ratio. These in situ XRD studies therefore support alloy formation with a stoichiometry ratio of platinum:tin of 1:1. The tin in excess of that needed to form this alloy is present in an X-ray "amorphous" form, and is postulated to be present in a shell layer with a structure similar to that of tin aluminate.

A series of catalysts were prepared to contain 1 weight per cent platinum, and tin to platinum ratios ranging from about 8:1, using a low (110 m²/g) and high (300 m²/g) surface area alumina (52). XRD studies indicated that, irrespective of the tin to platinum ratio, the only crystalline phase detected by XRD was platinum-tin (1:1). The XRD intensity of lines for the tin-platinum alloy phase increase with increasing tin to platinum ratios, indicating the presence of unalloyed platinum in the samples containing low tin loadings. The integrated intensity materials; the fraction of platinum present in an alloy phase increases with increasing tin concentration and only approaches complete alloy formation at tin:platinum ratio ≈ about 5.

Platinum-tin supported on silica exhibits much different behaviour than when it is supported on alumina. As reported by others, it is easier to reduce tin to the zero valent state when silica is used as the support (49).

For platinum supported on a co-precipitated tin oxide-alumina catalyst, alloy formation occurs to a much smaller extent than it does on a material prepared by impregnation with the chloride complex (48, 49). Since most commercial catalyst formulations are based on tin/alumina co-precipitated support materials, it appears that the studies using platinum and tin co-impregnation techniques, while interesting, are not directly applicable to the commercial catalysts.

Platinum Metals Rev., 1992, 36, (3)
Fig. 8 Diffraction peak positions and relative intensities for (a) Pt (f.c.c.), (b) Pt-Sn (h.c.p.), (c) a reduced Pt-Sn/alumina catalyst with 5 wt. per cent platinum, and (d) reduced Pt-Sn/alumina catalyst with 0.6 wt. per cent platinum.

Measured for the most intense PtSn peak (102) is plotted versus the tin content on the high and low surface area supports in Figure 9, and clearly shows that the amount of platinum present as crystalline alloy increases with increasing tin:platinum ratios. Also, the crystallite size, calculated from the XRD data, shows that the diameter of the crystallite increases from about 10 to 16 nm with increasing tin content.

X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure spectra (EXAFS) were obtained for a series of tin-platinum on alumina or silica samples (53, 54). X-ray fluorescence and absorption spectra, at the platinum LIII, and tin K-edges, were recorded for dried, calcined and reduced (at 773 K and 1 bar hydrogen) preparations of tin-platinum loaded on silica and alumina supports. The platinum was maintained at 1 weight per cent and the tin content was varied from 0.39 to 3.4 per cent.

The near-edge profiles at the platinum LIII and tin K-edges did not show any distinctive features for any of the reference substances or the various catalyst preparations. However, the steep increases in absorption appear at different locations; all edge positions were measured relative to those of the corresponding metal foils, assigned as zero. Typical resolved near-edge profiles are illustrated in Figure 10. The resolved peak height is a measure of its ionicity; that is for platinum the number of 5d electrons removed by chemical-bond formation. Horsley showed that the areas of the threshold resonance lines can be estimated by deconvoluting the absorption edge into a Lorentzian.

Fig. 9 The integrated intensity measured from the 100% Pt-Sn (102) profile versus Sn content: • on the United Catalysts, Inc. alumina support and ▲ on Degussa alumina support.
Fig. 10 Profiles at the Pt LIII edge, resolved into overlapping Lorentzian and tan⁻¹ functions. The large dots show how well the recorded data (—) are reproduced by the sum (....) of the functions (....)

Fig. 11 Radial distribution functions derived for the calibrating materials: (a), (b), (c) at the platinum LIII edge, and (d), (e), (f) at the tin K-edge

Fig. 12 Peak positions (not corrected for phase shift) are indicated by vertical lines, with approximate peak heights, derived from EXAFS spectra at the Pt LIII edge, for several reference compounds and the six catalysts listed in Table II:

(a) Pt-Sn alloy;
(b) Pt metal;
(c) PtO₂;
(d) PtCl₅·2H₂O (—) and H₃PtCl₆ (....);
(e) dry preparations: B (—) and F (....);
(f) calcined preparations: B (—) and F (....);
(g) reduced samples: A (—) and D (....);
(h) reduced samples: B (....) and E (....);
(i) reduced samples: C (—) and F (....)
Table II
Catalyst Compositions

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Support</th>
<th>Platinum</th>
<th>Tin</th>
<th>Chlorine</th>
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<tbody>
<tr>
<td>A</td>
<td>Alumina</td>
<td>1.0</td>
<td>0.44</td>
<td>&gt;1.2</td>
</tr>
<tr>
<td>B</td>
<td>~250 m²/g</td>
<td>1.0</td>
<td>1.47</td>
<td>&gt;1.2</td>
</tr>
<tr>
<td>C</td>
<td>Silica</td>
<td>1.0</td>
<td>3.40</td>
<td>&gt;1.2</td>
</tr>
<tr>
<td>D</td>
<td>Silica</td>
<td>1.0</td>
<td>0.39</td>
<td>&gt;1.2</td>
</tr>
<tr>
<td>E</td>
<td>~700 m²/g</td>
<td>1.0</td>
<td>0.51</td>
<td>&gt;1.2</td>
</tr>
<tr>
<td>F</td>
<td></td>
<td>1.0</td>
<td>0.78</td>
<td>&gt;1.2</td>
</tr>
</tbody>
</table>

component and an underlying "step", which represents the onset of absorption due to a continuum of states (55). In general, it was found that increasing the tin loading on either support decreased the d band vacancy for tin. In contrast, alloying platinum with tin leads to an increase in the d band vacancies. Overall, alumina favours a higher d band vacancy than silica does. These results are in general agreement with those reported by Meitzner and co-workers (49).

The peaks in the radial distribution functions (RDF) for the reference compounds, after background and termination error corrections, provide the basis for assignments of the catalyst RDFs. For reference, RDFs for PtO₂, H₂PtCl₆ and platinum-tin alloy, derived from EXAFS at the platinum L₃-edge, and of SnO, SnCl₄·5H₂O and the platinum-tin alloy, derived from EXAFS at the tin K-edge, are reproduced in Figure 11. Examination of the RDFs derived from the two sets of scans for the six preparations show both similarities of local structures and striking differences which may be ascribed to control by the supports. In the following text reference will be made to a "stick" diagram (Figure 12), presented to illustrate the distribution of atom-pair distances, plotted as derived, without correcting for phase shifts. A figure of data for the tin K-edge that parallels the data for platinum shown in Figure 12 can be found in Reference 54.

The tin K-edge spectra indicate that the arrangement of atoms about the tin species is essentially the same for both the high area alumina and high area silica supports. Sn-O atom pairs dominate even after reduction, but their contribution decreases somewhat with increasing tin loading. Reference to Figure 12 shows that the two supports lead to a profound difference in configurations of atoms about the platinum. There is a somewhat mysterious 2.5 Å peak in the dried sample for the two supports (spectrum a, Figure 12) and for the reduced sample C (spectrum e, Figure 12). This peak has been assigned to platinum-tin, as present in the alloy (49).

However, its appearance in the oxidised states of these preparations suggests that a more plausible assumption might be the presence of a solid solution of the oxide, which is incompletely decomposed by calcining or reduction.
An electron microdiffraction technique was employed to identify crystal structures developed in two platinum-tin/alumina catalysts (56). One catalyst was prepared by co-precipitating tin and aluminium oxides and then impregnating the calcined material with chloroplatinic acid to give a platinum:tin atomic ratio of 1:3. The second catalyst was prepared by co-impregnating Degussa alumina with an acetone solution of chloroplatinic acid and stannic chloride to provide a platinum:tin ratio of 1:3. Platinum-tin alloy was not detected by X-ray diffraction for the co-precipitated catalyst although evidence for platinum-tin alloy was found for the co-impregnated catalyst. A representative transmission electron micrograph is shown in Figure 13. Electron microdiffraction studies clearly show evidence for an alloy phase with a platinum:tin ratio of 1:1 in both catalysts. Evidence for minor amounts of alloy with a platinum:tin ratio of 1:2 (for example PtSn, alloy phase) was also found for the co-precipitated catalyst.

EDX data were obtained for a number of the metal particles present in the two catalysts. The data in Figure 14 represent EDX traces from four small individual particles that are representative of those in the catalyst prepared by co-impregnation with the platinum and tin complex; it is clear that both platinum and tin are observed in each of the particles. Platinum and tin EDX areas were measured for a number of metal particles. The fraction of particles present with various tin:platinum ratios versus the tin:platinum ratio for the co-impregnated catalyst is shown in Figure 15; it is evident that the dominant tin to platinum ratio is 1:1. Considering the uncertainty in the EDX data, it is concluded that the data in Figure 15 are consistent with the finding of an alloy composition of tin:platinum of 1:1, as was obtained by XRD.
The EDX data for the co-precipitated tin- and aluminium-oxide give contrasting results. As can be seen in Figure 16, the metal particles large enough for EDX analysis (about 4.0 nm or larger) consist solely of platinum; only rarely is it possible to find a metal particle that contains both platinum and tin. It is therefore concluded that the majority of platinum is present as metallic platinum, and not in an alloy form. As noted above, a few particles were found having a microdiffraction pattern consistent with a platinum:tin ratio of 1:2; it is believed that this composition may be the result of platinum being located on a very few tin rich, or pure tin oxide, regions that were formed during the co-precipitation.

Data from transmission electron microscopy (TEM) show that there are two contrasting structures for alumina supported catalysts of a given tin:platinum chemical composition: one structure is obtained for a co-precipitated material and another for a co-impregnated material. For the co-impregnated material both the tin and platinum are located upon the alumina surface following reduction at about 500°C; the migration of tin or platinum to the bulk does not occur to a measurable extent. Following calcination, most, if not all, of the tin is present in a surface egg-shell layer that chemically resembles a tin aluminate. In forming the tin aluminate some of the tin chloride is converted to a complex that contains more chloride as, for example:

$$2 \text{SnCl}_2 \rightarrow \text{Sn}^{2+} + \text{SnCl}_4^{2-}$$

Upon reduction some of the tin, if present initially as tin(IV), is converted to tin(II) and tin(0); the fraction of tin that is reduced to tin(0) depends upon the amount of tin in the catalyst. The higher the tin loading, the higher the number of moles (but not necessarily the fraction) of tin that is present in the zero valent state. The amount of platinum-tin alloy will then depend upon the total amount of tin, relative to platinum, that is present in the catalyst; the greater the amount of tin the...
greater the amount of platinum-tin alloy. Thus, we believe that the co-impregnated catalyst consists of chlorostannate complex(es), a surface compound(s) that resembles a tin aluminate, and a mixture of platinum and platinum-tin alloy; the ratio of platinum to platinum-tin alloy will depend upon the composition of the catalyst.

The co-precipitated catalyst differs drastically from that of the co-impregnated catalyst. For the co-precipitated material, a significant, or even a major portion, of the tin will be present in the bulk of the alumina support material; hence, the surface concentration of tin, for a common tin to aluminium ratio, will be much lower for the co-precipitated catalyst. For the co-precipitated material there will be isolated tin ions on the surface of the support; the concentration of these will depend upon the tin to aluminium ratio. Little, if any, of these isolated tin ions will be reduced to the metal; the small amount of tin(0) present is most likely due to the reduction of the few nearly pure tin oxide particles formed during co-precipitation. Upon reduction, nearly all of the platinum will therefore be present as isolated platinum atoms or as platinum metal crystallites. It is postulated that the tin in the co-precipitated material acts as a trap that retards platinum crystal growth, much as was proposed in Reference 4 for another catalyst system.

Thus, we consider the surface of the co-precipitated material to be as shown by the schematics in Figures 17 and 18.

The schematic for a co-impregnated alumina with a low tin to platinum ratio (1:1, in Figure 17) indicates that most of the platinum is present as metallic platinum with some platinum-tin alloy, and that most of the tin is present as the "tin aluminate" compound. For the high tin-platinum co-impregnated catalyst (tin:platinum equals 12:1) a large fraction of the tin can still be regarded as being present as the "tin aluminate" but, because of the larger amount of tin present, sufficient tin(0) is found to convert nearly all of the tin to platinum-tin.

For the co-precipitated catalyst, the schematic representation (Figure 18) indicates that nearly all of the tin on the surface is present as isolated tin(II) — or tin(IV) — ions. The platinum is therefore present as small platinum crystallites. It is speculated that the tin ions serve to "trap" platinum crystallites and retard platinum crystal growth. In this case there should be an optimum where the number of tin ions is about equal to the number of platinum atoms. Thus, the idealised co-precipitated catalyst would consist of isolated tin ion-platinum particles.

The chloride has not been included in the above schematics. The Mössbauer and XPS data indicate that it is likely to be present as SnCl$_4^{2-}$, SnCl$_2^{2-}$ and AlOCl or AlCl$_4^{-}$-type complexes. Presumably, these ionic complexes would be highly dispersed both on the surface and in the bulk. The XPS and SEM data clearly indicate that at least a portion of the chloride is mobile during calcination and reduction.
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Fifth Autocatalyst Plant Commissioned

JOHNSON MATTHEY OPENS NEW FACILITY AT GERMISTON

On the 26th March, 1992 Johnson Matthey’s latest Autocatalyst Plant was officially opened by the British Ambassador to South Africa, Sir Anthony Reeve, K.C.M.G., bringing to five the number of autocatalyst plants now operated by Johnson Matthey worldwide. The facility is situated in Germiston South, some 20 km from Johannesburg and a mere 7 km from Wadeville where Johnson Matthey first began operations in South Africa almost 40 years ago.

The establishment of this plant creates a further chapter in Johnson Matthey’s participation in South African industry and brings to the country the high technology associated with the manufacture of platinum metals-containing autocatalysts, so adding value to locally produced materials. The plant has a capacity of one million autocatalysts per shift per year, and at the present time the total output is destined for export under the South African Government’s “Phase VI” of the motor industry’s local content programme, under the terms of which the industry is encouraged to export motor components, catalytic converters falling within this category.

At present there are no stringent local requirements covering motor vehicle emissions, which must await the availability of unleaded fuel in 1995, when a domestic market for autocatalysts will develop.

Johnson Matthey’s new facility consists of 10,000 square metres of covered area, a third of which is occupied by the autocatalyst plant. It also houses the Chemical Salts Production Unit, which primarily supplies the requirements of the autocatalyst facility, and Johnson Matthey’s Noble Metals business. This produces and refines rhodium-platinum catalyst gauze for the nitric acid industry, Johnson Matthey thereby playing a strategic role in the mining and agricultural industries of South Africa. The local requirements for platinum apparatus are also satisfied by this unit.

R.A. Simpson
ABSTRACTS
of current literature on the platinum metals and their alloys

PROPERTIES

Kerr Enhancement by Layer Modulation in Co/Pt Multilayers
Layer modulated Co/Pt multilayers were studied to achieve perfect squareness for ultrathin films, even with a thickness ratio \( t_{Co}/t_{Pt} = 1 \), and to attain a large Kerr rotation angle. Good degree of hysteresis was obtained by decreasing the number of repetitions \( n \) in \((5Pt/5Co)_n/100Pt\) multilayers. The \((5Pt/5Co)\), multilayers with good squareness were stacked through a Pt interlayer of various thicknesses, giving excellent magneto-optical properties. A Pt interlayer > 30 Å gave characteristic hysteresis with good squareness.

Transformation of Platinum Carbonyl Clusters on Graphite under Laser Irradiation and Their Scanning Tunneling Microscopy Observation
STM images were obtained from an isolated aggregate of Pt carbonyl clusters \([\text{NEt}_4]_2[\text{Pt}_{12}(\text{CO})_{24}]\), which were adsorbed from the tetrahydrofuran solution onto the surface of a freshly cleaved highly oriented pyrolytic graphite under a \( N_2 \) atmosphere. The morphological changes of the surface bound Pt carbonyl clusters were observed under pulse laser irradiation resulting in the effective decarbonylation and fragmentation. The Pt carbonyl clusters were converted to a highly dispersed Pt microcrystalline.

Palladium-Zirconia Diffusion Bonds: Mechanical Properties and Interface Reactions
High strength and toughness diffusion bonds have been made using Pd foils between TZP zirconia blocks at temperatures > 1000°C only in vacuum. Bonds made at < 1000°C in vacuum and all air conditions had negligible strength. Strong bonds made in vacuum lost almost all their strength on annealing in air at > 1000°C. Anneals in vacuum resulted in a decrease in bond strength, but with a much less marked effect. Pd-ZrO\(_2\) interfaces have been characterised by TEM and a thin reaction zone identified, which contains Pd, Zr and O in ratio 30:52:18. Evidence for the presence of a liquid phase at the Pd-ZrO\(_2\) interface during bonding is presented. The perfection of the bonded interface determines the strength and toughness of the bonds.

Anisotropy in a Heavy Fermion Superconductor: UPd\(_2\)Al\(_3\)
The anisotropy of magnetisation, electrical resistivity and upper critical magnetic fields of UPd\(_2\)Al\(_3\), are reported. The magnetisation curve in the antiferromagnetically ordered state shows large anisotropy, indicating that the sublattice moments lie in the basal hexagonal plane. The upper critical magnetic field was rather isotropic, whereas it was strongly anisotropic in UPt\(_3\), and the anisotropy in the magnetisation in the normal and antiferromagnetic state of UPd\(_2\)Al\(_3\), was also larger.

Preparation of a Large Al\(_{13}\)Pd\(_9\)Mn\(_{10}\) Single-Quasicrystal by the Czochralski Method and Its Electrical Resistivity
A seed single-quasicrystal of AlPdMn was grown by the Czochralski method, after choosing a liquidus of composition I-Al\(_{13}\)Pd\(_9\)Mn\(_{10}\) which equilibrates to the stoichiometricicosahedral(I) phase. The maximum size of the ingot reached was 10 mm in diameter and 50 mm long. The electrical resistivity of the crystal has a negative temperature dependence in the range 40–270 K, and has a maximum value of 65–107 \( \mu \Omega \)m at \( -40 \) K.

Possible 4d Ferromagnetism of Rh and Ru Overlayers on a Ag(001) Substrate
The possibility of 4d ferromagnetism of Rh and Ru overlayers on a Ag(001) substrate was studied using the full-potential linearised augmented-plane-wave method. The ferromagnetism of Rh/Ag(001) could be destroyed by an additional Ag layer whereas Ru/Ag(001) was predicted to be ferromagnetic with both a larger magnetic moment and larger magnetic energy even after being covered by a Ag layer.

Resistivity and Thermopower Studies in Ce(Ru\(_{1-x}\)Cu\(_x\))\(_2\)Si\(_2\) Systems
Resistivity \( \rho \) and thermopower S studies at 1.7–300 K on Ce(Ru\(_{1-x}\)Cu\(_x\))\(_2\)Si\(_2\) alloys were performed. Variation of x provided a means for controlling the single-site and inter-site coupling strengths and to check whether magnetic order developed in the limit of \( x \to 0 \) or 1. The \( \rho \) and \( S \) curves showed features that could be identified with the Kondo temperature.
Plasma Etching of RuO₂ Thin Films


The plasma etching of RuO₂ thin films was performed using CF₄ or O₂ plasma, and compared with sputter etching. O₂ plasma radicals, using ion impact, were more effective at etching than radicals from CF₄, and a higher etching rate and good selectivity were obtained. The plasma etching rate was higher than for sputter etching, giving fine patterns.

CHEMICAL COMPOUNDS

Ba₅Ru₃Ta₂O₁₀Br₂ — Synthesis and Structure Characterisation of a New Oxide-Bromide with Ruthenium


A new compound Ba₅Ru₃Ta₂O₁₀Br₂ was prepared by BaBr₂ flux. Crystal structure studies showed that it crystallises with rhombohedral symmetry, and lattice constants \( a = 5.981(1) \) Å and \( c = 60.79(2) \) Å; \( Z = 3 \). It is described by a 24-layer structure of Ba⁺⁺⁺ /O⁻⁻⁻ and Ba⁺⁺⁺ /Br⁻ with incorporated Ru⁺⁺⁺ and Ta⁺⁺⁺ ions forming (Ru₂Ta₃)O₆ groups which are corner connected by RuO₂ octahedra.

ELECTROCHEMISTRY

Electro-oxidation of Methanol on Graphite-Supported Perovskite-Modified Pt Electrodes in Alkaline Solution


Graphite-supported perovskite-modified Pt electrodes showed much higher electrocatalytic activities than smooth Pt or graphite-supported Pt electrodes towards MeOH electro-oxidation in 1 M NaOH solution at 25°C with zero-current potential as low as 200 mV versus the reversible H electrode. The catalytic activities of the modified electrodes were very stable and remained unaffected towards the poisoning effect of CO. CO and MeOH could be oxidised simultaneously and MeOH oxidation was enhanced at high positive potentials by the presence of CO.

A Microelectrode Study of Oxygen Reduction at the Platinum/Recast-Nafion Film Interface


The electrochemical reduction of O₂ at a Pt microelectrode under a range of humidification conditions and temperatures, in a cell containing a hydrated recast Nafion film as the only electrolyte is reported, the conditions being identical to those in a polymer electrolyte fuel cell. The interfacial rate of O₂ reduction near 0.9 V was similar for the Pt/recast ionomer interface and for Pt immersed in dilute aqueous acid solutions. A significant loss of O₂ reduction activity occurred when the recast ionomer electrolyte loses H₂O.

Ruthenium-Catalysed, Electrochemical Cleavage of Aryl Olefins for the Synthesis of Benzaldehydes


A one-pot, one-step cleavage of electron-rich double bonds to the corresponding aldehydes, such as 3,4-methylenedioxy-1-(1-propenyl)benzene and related compounds, using a RuSiW₉O₃⁻⁻⁻ catalyst in an electrochemical two-phase double mediator system or with stoichiometric regeneration is reported. Up to 200 turnovers of the catalyst could be obtained without any loss of activity of the system.

Formation of Hypochlorite, Chlorate and Oxygen during NaCl Electrolysis from Alkaline Solutions at an RuO₂/TiO₂ Anode


The current efficiency for hypochlorite, chlorate and O₂ formation at a RuO₂ /TiO₂ anode were determined under various conditions in order to optimise the electrolytic cell and electrolysis conditions for weak alkaline solutions of NaCl for on-site disinfection. At 298 K, solution flow velocity of 0.075 m/s and high current density, hypochlorite formation was determined by mass transfer of chloride. The formation of chlorate is ascribed to the direct oxidation of chloride to chlorate and hypochlorite conversion.

PHOTOCONVERSION

Photodissociation and Photodesorption of O₂ Adsorbed on Pd(III)


The dynamics of the UV-photochemistry of molecularly adsorbed O₂ on Pd(III) was studied using pulsed laser light at 3.9–6.4 eV photon energy. Upon UV-irradiation (hv>3.5 eV) O₂ dissociates to form surface O and desorbs with translational energies exceeding the surface temperature. Displacement processes occurred causing conversion between molecular binding states and thermally accommodated desorption. All processes share a common dependence on photon energy in the form of an exponential rise by a factor of 35 between 3.9–6.4 eV.

Photochemistry of Adsorbed States of Diazirine on Pd(110)


XPS studies of adsorbed states of diazirine on Pd(110) showed that it is possible to correlate the CN and NN photoduced bond breaking processes in diazirine on Pd(110) with the initial different chemisorption state of the molecule. Photodissociation of π-chemisorbed diazirine results in NN bond cleavage.
Photoredox Properties of [OsN(NH₃)₃]³⁺ and Mechanism of Formation of [(Os(NH₃)₃(CH₃CN))₂N₂]³⁺ through a Nitrido-Coupling Reaction


The oxidation of [Os(NH₃)₃]Cl³⁺ by Ce⁴⁺ in H₂O gave [Os(NH₃)₃]⁺ quantitatively, and excitation of (1) in the solid state or in solution at 300-400 nm resulted in room-temperature photoluminescence. Photolysis of (1) in the presence of an electron donor in acetonitrile yielded the dinitrogen product [(Os(NH₃)₃(CH₃CN))₂N₂]³⁺ (2). Oxidation of (2) by Ce⁴⁺ in H₂O followed by precipitation with HCl gave the product [Os(NH₃)₃]Cl⁻ in detectable yield.

pH Control of Photoreactivity of Ru(II) Pyridyltriazole Complexes: Photoinduced Linkage Isomerism and Photoanation


The photophysical and photochemical behaviour of mixed ligand complexes of Ru(II) with 3-(pyridin-2-yl)-1,2,4-triazole (HPTN) were studied in solutions of various acidities. Promotion of both the N-2 bound (HPTN-2) and the N-4 bound (HPTN-4) isomers of [(bpy)₂Ru(HPTN)]⁺ resulted in a decrease in the luminescence lifetime in solution and an increase in reactivity upon photolysis in CH₂Cl₂. Photolysis of either protonated isomer in CH₂Cl₂ resulted in linkage isomerism.

ELECTRODEPOSITION AND SURFACE COATINGS

Studies of Palladium Electrodeposition from Baths Based on Pd(NH₃)₂X₂ Part II. X = Br and X = NO₃


The chemistry and electrochemistry of electroplating baths based on Pd(NH₃)₂Br and Pd(NH₃)₂(NO₃)₂ were studied and compared with that of Pd(NH₃)₂Cl₂. The electroactive species in all the baths was Pd(NH₃)₂⁺ but only in bromide electrolytes did Pd dissolve anodically.

Ultrahigh Vacuum Chemical Vapor Deposition of Rhodium Thin Films on Clean and TiO₂-Covered Si(111)


Thin film deposition by thermal decomposition of Rh(CO)₅(H₂O)₅ has been studied under UHV conditions. Thin films were deposited on clean Si(111)-(7 × 7) and TiO₂-covered Si(111) substrates, and analysed. Rh films deposited at 200-500°C contain C and O impurities. The C and O incorporation is more severe in the initial deposition stage on a clean Si surface than on a growing surface.

APPARATUS AND TECHNIQUE

Use of the Electroreflectance Technique in Pt/GaAs Schottky Barrier Sensor Characterization


A new way to measure the gas sensitivity of a sensor based on a Pt/GaAs Schottky diode by measuring the electroreflectance spectra is reported. The electroreflectance spectra were obtained and analysed as a function of the device exposure to a H-containing atmosphere at different temperatures. The results obtained indicated that the H-induced modification of the spectra can be viewed as a barrier height lowering of about 0.2 eV.

Ammonia Sensitivity of Pt/GaAs Schottky Barrier Diodes. Improvement of the Sensor with an Organic Layer


A sensor for the detection of NH₃ over a wide temperature range has been developed which utilises a Schottky barrier device Pt/n-GaAs with a porous discontinuous Pt film and a layer of polyetherimide. The organic layer increases the sensitivity of the device and may allow the sensor to be used in aqueous solution and with biological material. The detection limit of the device in synthetic air is 10 ppm of NH₃.

Infrared Response of Pt/Si/ErSi₁₋₀.₇ Heterostructure: Tunable Internal Photoemission Sensor


An internal photoemission response of a Pt/Si/ErSi₁₋₀.₇ heterostructure is reported. With this device the photoresponse can be strongly modified when a bias of a few hundred mV is applied between the two metallic electrodes: the cutoff wavelength is shifted from 1.4 µm to >5 µm, and the quantum efficiency is increased up to 5% at a wavelength of 1.2 µm when a positive bias is applied to the front Pt electrode.

Efficient Palladium Isotope Chromatograph for Hydrogen (EPIC)


An apparatus was designed to separate a H flow into deuterium and protium, in an efficient Pd isotope chromatograph (EPIC), using 48 wt.% Pd deposited on Al₂O₃ packed into a column 6.8 mm i.d. × 910 mm long. Design modifications to permit operation with tritium, increased throughput and improved product purity are discussed.
Considerations of the pH Dependence of Hydrous Oxide Films Formed on Iridium by Voltammetric Cycling


The magnitude of the charge storage capacity attained by Ir oxide electrodes under potential cycling conditions is important for the ratio of protons to electrons participating in the potential-determining equilibria under zero current conditions. A model based on electron exchange between protons in solution and conductive sites on the hydrous oxide surface is proposed; electrochemical cycling of Ir can make simple, robust solid state pH electrodes.

Chemiluminescence Detection Using Regenerable Tris(2,2'-bipyridyl)ruthenium(II) Immobilized in Nafion


A detection method based on the electrogenerated chemiluminescence of tris(2,2'-bipyridine)Ru(II), (Ru(bpy))$_2^{2+}$, immobilised in a Nafion film coated on an electrode is described. The sensor is used in flow injection to determine oxalate, alkylamines and NADH. Detection limits are 1 μM, 10 nM and 1 μM, respectively, with working ranges extending over 4 decades in concentration. Sensitivity is constant over pH 3–10.

Determination of Nitrite Based on Medicated Oxidation at a Carbon Paste Electrode Modified with a Ruthenium Polymer


The mediated detection of nitrite by C paste electrodes modified with [Ru(bpy)$_3$](PVP)$_m$ClCl is described. The Ru surface modifier substantially lowers the overpotential for nitrite oxidation, thus allowing its determination at a lower potential. Standard calibration curves yielded slopes of 0.3 μA/μM over the linear range 5 × 10$^{-4}$–5 × 10$^{-3}$ M nitrite, with a detection limit of 3 × 10$^{-3}$ M (1.38 ppb).

**HETEROGENEOUS CATALYSIS**

Reforming of Pyrolysis Gasoline over Platinum-Alumina Catalysts Containing MFI Type Zeolites


Reforming of pyrolysis gasoline was carried out over Pt/Al$_2$O$_3$ catalysts containing small amounts of pentasil zeolite of the MFI type. The addition of these zeolites lowered the coke deposition on the catalysts giving products almost free of aliphatics. The pressure was kept low enough to achieve a significant increase in the concentration of aromatics.

Change of the Valnet State of Metals in the Film of the Pd-Pt/Al$_2$O$_3$ Catalyst during Heating in Air and Deep Methane Oxidation


Studies of a mutual effect of Pt and Pd on the stability of their different valent states in bimetallic catalysts Pd-Pt/Al$_2$O$_3$ during heating in air and deep CH$_4$ oxidation at 600–700 K were performed on bimetallic Pd-Pt catalysts prepared by deposition of PtCl$_4$ and H$_2$PtCl$_6$ solutions on γ-Al$_2$O$_3$. In the reaction mixture CH$_4$–air at 600 K, the valent state of Pt changed from Pt$^0$ to Pt$^{2+}$ but in the presence of Pt oxidised forms, Pt$^+$ stabilised the catalyst. Pd-Pt/Al$_2$O$_3$ catalyst showed high activity and stability.

Catalytic Etching of Pt/Rh Gauzes


Gauzes made of 90% wt.% Pt/10 wt.% Rh were catalytically etched in H$_2$/O$_2$ mixtures. The gauzes etched over exactly the same range of temperatures and gas stoichiometries as pure Pt. However, pure Rh etched in neither pure gases nor under reaction conditions. In a laminar flow type reactor weight loss in the gauzes was significant, indicating rapid etching, with smooth surfaces similar to those of untreated material. However, in an impinging jet reactor there was little weight loss, but the surfaces were partially covered by complex particle structures, 1–10 μm.

Hydrogen Formation in Propane Oxidation on Pt-Rh/CoO$_2$/Al$_2$O$_3$ Catalysts


TPO of propane at 200–550°C was carried out on PtRh/CoO$_2$/Al$_2$O$_3$ catalysts with O-deficient CoO$_2$ and H$_2$O gas shift reaction is the fast reaction.

Synthesis of Liquid Hydrocarbons from CO and H$_2$ over Co-Ru and Co-Pd Catalysts Supported on Alumina


Studies of the effect of additions of 0.1–0.5% Pd or Ru into 10% Co/Al$_2$O$_3$ catalyst on its activity and selectivity showed that bimetallic systems produced higher CO and C$_2$ + hydrocarbon yields. The Co-Ru catalysts were highly selective (≥ 80%) during the studied synthesis. When Pd or Ru were introduced into Co/Al$_2$O$_3$ catalysts, they allowed Co reduction at lower temperature and formation of Co aluminates.
Hydrogenation Activity of an Amorphous Pd-Zr Alloy Held in an Alumina Matrix

A catalyst of amorphous Pd-Zr alloy on an Al₂O₃ matrix was used to hydrogenate benzene, and its activity was compared to that of Pd-Zr cut into 1 mm fragments. The alloy fixed in Al₂O₃ had higher activity and also a smaller catalyst fouling rate than the alloy fragments. The Pd was considered to be well dispersed on the Zr oxide by the fixation of the amorphous alloy fragments. The Pd was considered to be well dispersed on the Zr oxide by the fixation of the amorphous alloy fragments. The Pd was considered to be well dispersed on the Zr oxide by the fixation of the amorphous alloy fragments. The Pd was considered to be well dispersed on the Zr oxide by the fixation of the amorphous metal complexes showed the highest activity in hydrodehalogenation of p-bromotoluene via H₂ and hydroxides of Cs, K and Na ions were effective promoters. Synthesis rate was greatest when the Cs:Ru ratio was 1.0, where activity was 20 times as high as that prepared from RuCl₃ .

Structure and Catalytic Activity of Metal Complexes Fixed on Supports. 5. A Catalyst of Amorphous Pd-Zr Alloy on an Al₂O₃ Matrix

Spectroscopic studies of the structure and activity of RhII complexes with various ligands immobilised on γ-aminopropyl containing silicate gel (γ-AMPS) and on polymers containing 3(5)-methylpyrazole and imidazole groups showed a substitution of the ligands on amino groups of the support that occurred in acetonitrile and hexafluorocacetelacetonato complexes. [Rh(1-OC₃H₅)₂] complex immobilised on γ-AMPS metal complexes showed the highest activity in hydrodehalogenation of p-bromotoluene via H₂ transfer from NaBH₄ and propanol-2.

Preparation and Characterization of Chlorine-Free Ruthenium Catalysts and the Promoter Effect in Ammonia Synthesis. 1. An Alumina-Supported Ruthenium Catalyst. 2. A Lanthanide Oxide-Promoted Ru/Al₂O₃ Catalyst. 3. A Magnesia-Supported Ruthenium Catalyst

Ru/Al₂O₃ catalyst prepared from Cl-free Ru carbonyl was much more active for NH₃ synthesis under 1.01 bar N₂ + 3H₂ than that prepared from RuCl₃. The high activity was related to the high dispersion and lack of Cl⁻. Oxides and hydroxides of Cs, Rh and K ions were effective promoters. Synthesis rate was a maximum for Cs:Ru=10. La(NO₃)₃, Ce(NO₃)₃, and Sm(NO₃)₃ were more effective promoters of NH₃ synthesis than Ca(NO₃)₂. MgO, Na₂O-MgO and Al₂O₃-MgO supports were most effective for NH₃ synthesis using Ru₄(CO)₁₉ as catalyst precursor, possibly due to high Ru dispersion. Alkali metal nitrates were the most effective promoters, and the synthesis rate was greatest when the Cs:Ru ratio was 1.0, where activity was 20 times as high as that without Ca(NO₃)₂ at 588 K.

HOMOGENEOUS CATALYSIS
Isomerization of Alkynemono-ols Catalyzed by Palladium(0) Complex and Diols

Studies of the isomerisation of various alkynemono-ols by Pd(dba), CH₃CO₂H, +Pr,P+ + HOCH₂CH₃ OH catalytic system in acetonitrile showed that it occurred under the milder reaction conditions of acetonitrile reflux temperature, when a catalytic amount of diols was added; α,β-unsaturated ketones were formed. ¹H NMR spectra showed the formation of two isomers, (E)-α,β-enones and β,γ-enones in the ratio of 4:1. This route gives a neutral, mild and convenient method for preparation of enones from the isomerisation of alkynemono-ols.

Synthesis of Sterically Hindered Biaryls via the Palladium-Catalyzed Cross-Coupling Reaction of Arylboronic Acids or Their Esters with Haloarenes

Sterically hindered arylboronic acids such as mesitylboronic acid were cross-coupled with 2-substituted haloarenes in high yields in the presence of Pd(PPh₃)₄ and aqueous Ba(OH)₂ in 1,2-dimethoxyethane. An alternative method using esters of boronic acids and K₂PO₄ in dimethylformamide was also developed for the cross-coupling reaction of arylboronic acids which were sensitive to hydrolytic deboronation with aqueous base.

Rhodium(I) Complex-Catalyzed Hydrosilylation of Dimethyl Mucnates

Complete regioselective 1,6-hydrosilylation of dimethyl cis,cis-muconate occurred by using trialkylsilanes in the presence of RhCl(PPh₃)₃ as a catalyst. The obtained functionalised ketene silyl acetal showed moderate electrophilic properties. Hydrosilylation of trans,cis-muconate resulted in a mixture of adducts but not a 1,6-adduct.

Direct Formation of Formic Acid from Carbon Dioxide and Dihydrogen Using the [{Rh(cod)(C1)}₂-Ph₂P(CH₂)_₄PPh₂ Catalyst System

Formic acid, isolable as Na formate from the reaction mixture, was produced directly from H₂ and CO₂ using a homogeneous catalyst system formed in situ from [{Rh(cod)(C1)}₂ and Ph₂P(CH₂)_₄PPh₂ with yields up to 1150 moles per mole of Rh. This in situ Rh catalytic system catalyses the reversible formation of formic acid from CO₂ and H₂ very efficiently, thus giving a way of activating CO₂ and/or storing H₂.
Studies of some dependences of dissolution of gaseous formaldehyde and paraformaldehyde in N,N'-dimethylacetamide were studied in a number of solutions during hydroformylation of CH₂O to glycolaldehyde in the presence of RhCl₄, 4H₂O and RhCl(PPh₃)₃ catalysts. The rate of achieving the stationary state depended on the H₂O content in the solvent and on the presence and composition of R complexes in the solution.

[Bi(Rh(CO))₄]⁻, [Bi₂(Rh(CO))₁₂]⁻, and Bimetallic Clusters as Catalysts for the Carboxylation of Nitrobenzene to Methyl Phenylcarbamate


Bimetallic clusters of general formula [PPN₂]₂[MRh₃(CO)₆] (M = Ru, Os or Fe; PPN⁺ = (PPh₃)₂N⁺) are active catalysts in the presence of MeOH for the carboxylation of nitrobenzene to methyl phenylcarbamate, but the addition of bipy (2,2’-bipyridine) greatly improves both rates and selectivities. The monometallic cluster [Rh₂(CO)₈]⁻ was more active and selective, and the monomer [Rh(CO)]⁻ even better.

Hydrodechlorination of Chloroaromatics: the Use of a Bifunctional Homogeneous Rhodium Catalyst for the Conversion of Chloroaromatics into Saturated Hydrocarbons


The catalytic conversion of chloroaromatics into the corresponding saturated hydrocarbons was catalysed by a bifunctional homogeneous Rh catalyst system generated from [C₆H₄(C₆H₅)RhCl₂]: in the presence of an excess of NEt₃, under 600 psi H₂ at 75°C.


A Rh catalyst mediated hydroformylation of glucal derivatives was achieved in good yields and selectivities using [Rh₂{(μ-S(CH₃)₂)NMe₃}(cycloclocta-1,5-diene)] and tris(ortho-tart-butylphenyl) phosphite as auxiliary ligands giving Z-formyl derivatives. The stereoselectivity of the reaction was determined by the stereochemistry of the allylic substituent when the formyl group entered at C 2.

The Osmium-Catalyzed Asymmetric Dihydroxylation: A New Ligand Class and a Process Improvement


The acceleration of osmate ester hydrolysis in the presence of organic sulphonamides and the discovery of a phthalazine class of ligands have led to a simple procedure for the Os-catalysed asymmetric dihydroxylation of olefins. This procedure is applicable to a wide range of olefinic substrates, and enantiomeric excesses > 90% for the resulting diols are obtained.

Ruthenium-Catalyzed Hydration of Nitriles and Transformation of δ-Keto Nitriles to Ene-Lactams


Hydration of nitriles and transformation of δ-keto nitriles to ene-lactams were performed efficiently by using RuH₂(PPh₃)₄ catalyst under mild conditions. In a typical case, the reaction of benzonitrile in 1.2-dimethoxyethane in the presence of 3 mol% of (1) at 120°C gave benzamide in 93% yield after filtration over Florisil.

FUEL CELLS

Electrode Reaction at Fixed Platinum Film—Fixation of Platinum Film on Stabilized-Zirconia Electrolyte and Its Effect on the Electrode Performance of the Solid-Electrolyte Fuel Cell


Sputtered Pt electrodes were fixed on yttria stabilised zirconia, YSZ, electrolyte by covering the electrode with a porous ceramic layer, so that the Pt film was kept stable and the resistance of the electrodes was very small. The polarisation behaviour was examined. Cathodic current increased as the Pt thickness decreased and anodic current increased as the ceramic layer thickness decreased.

CHEMICAL TECHNOLOGY

Basic Experimental Study on Palladium Membrane Reactors


Basic experiments on Pd membrane reactors, which use catalysts of 0.5 wt.% Pt on cylindrical Al₂O₃ pellets packed inside the membrane tube, were performed to explain the mechanism of H₂ permeation through the membrane, and to find the effect of the membrane surface on dehydrogenation using cyclohexane dehydrogenation as a model reaction.
ELECTRICAL AND ELECTRONIC ENGINEERING

Quality Dependence of Pt-n-GaAs Schottky Diodes on the Defects Introduced during Electron Beam Deposition of Pt


Current-voltage measurements performed on Pt Schottky barrier diodes (SBDs) deposited with and without shielding the n-GaAs substrate from stray electrons during electron beam metallisation showed that the use of a shield is essential if high quality devices have to be fabricated. The exposure of the semiconductor to stray electrons during metallisation caused non-ideal SBD properties.

Ballistic Electron Emission Microscopy Study of PtSi-n-Si(100) Schottky Diodes


Studies of PtSi-n-Si(100) Schottky contacts performed by BEEM for PtSi layers from 30–195 Å thick showed that Schottky barrier heights on the contacts followed mainly the values from the diode I-V characteristics. The ballistic transmission rate decreased with PtSi thickness and the average hot-electron mean free path in PtSi appeared to increase with thickness.

Shallow Ohmic Contact Formation by Sequential Deposition of Pd/AuGe/Au on GaAs and Rapid Thermal Annealing


Shallow ohmic contacts to n-GaAs were prepared by sequential deposition of Pd/AuGe/Au and rapid thermal annealing at 450–500°C for 30 s. The metallisation showed good electrical properties with a contact resistivity of 2 × 10−4 Ω cm². Using Pd to replace Ni in the conventional Ni/AuGe/Ni/Au structure as the first layer considerably reduced contact resistivities and gave good substrate adherence.

The Si/Pd(Si,Ge) Ohmic Contact on n-GaAs


A modified Si/Pd ohmic contact to n-GaAs of resistivity 2 × 10−4 Ω cm², has been developed, based on the solid-phase regrowth mechanism. A 15 Å layer of Ge or Si embedded in the Pd reduces the contact resistivity to 2–4 × 10−7 Ω cm² without loss of thermal stability. The reduction in the contact resistivity is explained by formation of a n+ GaAs surface layer via solid-phase regrowth. The modified contacts show uniform surface and interface morphologies, and contact resistivity stays in the mid-10−4 Ω cm² range after annealing at 400°C.

High-Reliability Interconnections for ULSI Using Al-Si-Pd-Nb/Mo Layered Films


A new Al-Si-0.3 wt.% Pd-0.4 wt.% Nb alloy and a bilayered interconnection using this alloy with Mo were investigated for ULSI interconnections. The electromigration lifetime of the alloy was 5 times better than that of Al-Si-0.5 wt.% Cu. When the new alloy was layered with Mo the electromigration resistance improved considerably, as compared to Al-Si-Cu layered with high-resistivity metal.

MEDICAL USES

The Dialysis Electrode—A New Method for in vivo Monitoring


The continuous measurement of neurotransmitter glutamate in the brain of a freely moving rat has been measured using an in vivo electrode. A working electrode of Teflon coated Pt wire with 4 mm Pt exposed at the end is inserted into the tip of a probe and the electrode is surrounded by a chosen enzyme, which is introduced by slow perfusion. The probe also contains a Ag/AgCl reference electrode.

Unwinding of Supercoiled DNA by Platinum-Ethidium and Related Complexes


A gel electrophoretic mobility shift assay was used to determine the unwinding of closed circular, supercoiled pUC 19 plasmid DNA induced by a variety of Pt complexes differing in their co-ordination mode to the double helix. Compounds included are the anticancer drug cisplatin and several of its analogues in which the organic intercalator ethidium is co-ordinated to Pt through an exocyclic amino group, and molecules in which 2 Pt centres are tethered by a polymethylene chain.

An Electrochemical Capillary Fill Device for the Analysis of Glucose Incorporating Glucose Oxidase and Ruthenium (III) Hexamine as Mediator


A method for measuring glucose based on enzymic oxidation and thin-layer bulk electrolysis using Ru(III) hexamine as mediator is described. The analysis is carried out in the electrochemical capillary fill device where sample enters the cell by capillary action and freeze-dried assay components, such as glucose oxidase, Ru(III)/hexamine and buffer salts, become solubilised and disperse throughout the cell.
NEW PATENTS

METALS AND ALLOYS

Sintered Ceramic Matrix-Metal Composite
JOHNSON MATTHEY P.L.C. British Appl. 2,245,557A
A compacted and sintered material consists of a matrix of ceramic grains of 0.5–1 μm in size, dispersed in which are 2–1000 nm particles of Pt, Pd, Ru, Mo, W or a mixture of these. The material has improved toughness and crack resistance, significant catalytic activity even though the metal is not exposed, and is used for cutting tools, catalysts, and components for internal combustion engines, for example cylinder liners and heads.

ELECTROCHEMISTRY

Low Overvoltage Cathodes for Chlor-Alkali Cells
DOW CHEMICAL CO. U.S. Patent 5,066,380
Electrolytic cathodes for chlor-alkali cells are manufactured by contacting a metal substrate with a solution of pH U.8 containing Ru, Rh, Ir, Os and/or Pt ions, especially Ru ions, and Pd ions. The Pd promotes enhanced deposition of the electrocatalytic metal, by non-electrolytic reduction, to give a mixture of the metal and Pd in hard, continuous non-dendritic form. The cathodes obtained have low overvoltage, tightly adherent coatings and improved electrocatalyst loading.

ELECTRODEPOSITION AND SURFACE COATINGS

Platinum Plating or Electroforming Bath
ELECTROPLATING ENG. European Appl. 465,073A
A plating bath consists of 2–100 g/l Pt from at least one Pt compound, 20–100 g/l alkali metal hydroxide, a compound selected from soluble carboxylates, phosphates and sulphates, and an alloying metal salt of Pd, Ir, Ru, Au or Ag. The bath is used for electroplating or electroforming at 65°C or more, at 1–3 A/dm², to give products of not more than 50 μm and at least 10μm thickness, respectively. Materials with high hardness, thickness and therefore improved corrosion and scratch resistance are obtained.

Rhodium Plated Copper Laminated Layered Plate for Slip Rings
NIPPON AVIONICS K.K. Japanese Appl. 3/223,486
A Cu laminated layered plate consisting of a base material, a resin insulating layer, and a Cu foil, is wet plated with Cu, Ni and Au, and then plated with Rh to give a 1.0–2.5 μm thick layer. Preferably soft etching using ammonium persulphate is effected between the Cu, Ni and Au plating steps.

Pore-Free Precious Metal Coating for Electrodes
TANAKA KIKINZOKU KOGYO Japanese Appl. 3/285,091
A Ti, Ta, Nb or precious metal electrode base is coated with an organo-Pt, organo-Ir or organo-Ru ink containing 1–100 wt.% of an organometallic resinate, 50 wt.% or less of resin and 80 wt.% or less of an organic solvent, followed by drying and firing. The method provides electrodes coated with a thin film of precious metal at a thickness of 0.5–1.5 μm.

Electroless Plating of Palladium-Silver Alloy Film
EBARA CORP. Japanese Appl. 3/287,781
A Pd-Ag alloy film is precipitated on a catalytically active carrier from a plating bath containing 0.001–0.500 mol/l (total) of Pd and Ag salts, 0.01–50 mol/l (total) of NH₃, and/or an amine compound, 0.0005–0.5000 mol/l of hydrazine and/or a hydrazinium salt as the reducing agent, and 0.001–10 mol/l of aminopolyhydric acetic acid and/or its salt as the chelating agent.

Electrolytic Deposition of a Palladium-Nickel Alloy Contact Layer
KONTAKT SPEZIAL GOR. East German Patent 292,596
A Pd-Ni alloy contact layer is deposited from an electroplating bath containing 10–15 g/l Pd and 5–10 g/l Ni as salts, preferably in ammonia solution, and 0.01–1.0 g/l of a polyfunctional 5-membered heterocyclic compound, added as an aqueous solution.

APPARATUS AND TECHNIQUE

Electrochemical Sensor for Monitoring Zirconium Alloy Corrosion
HITACHI K.K. Japanese Appl. 3/218,452
An electrochemical sensor for monitoring the corrosion of Zr alloy has a Zr alloy sample electrode, a membrane coated Ag-Ag chloride reference electrode, and a Pt counter electrode, all sealed in a ceramic mould, within a corrosion resistant stainless steel casing. The corrosion of Zr alloy in service is surmised from that of the sample alloy, and measurement of the corrosion current detects the state of deterioration of the environmental water quality.

High Durability Corrosion Sensor with Zinc-Platinum Galvanic Pair
NISSAN MOTOR K.K. Japanese Appl. 3/242,546
A sensor for monitoring corrosion rate for carrying out an accurate corrosion test consists of a Zn-Pt galvanic pair and a mechanism for removing Zn corrosion products to prevent deterioration of the galvanic pair. This gives a large signal level, and lowering of the signal by deposition of corrosion products can be prevented.

JOINING

Improved Soldering Material for Electronic Parts
KYOCERA CORP.  *Japanese Appl. 3/248,796*
A soldering material consists of Au, 0.1–15.0 wt.% In, and 0.1–5.0 wt.% of at least one of Pd, Rh, Co and Cr; with preferred materials containing 0.5–1.0 wt.% In and 0.1–1.0 wt.% Pd. The solder material has improved soldering strength (14.0 kg or higher), improved corrosion resistance, is free from electromigration, and is used for soldering outer leads.

HETEROGENEously CATALYTIC

Platinum Catalysts for Conversion of n-Butane to Isobutene
ENIRICERCHI S.P.A.  *British Appl. 2,246,524A*
Catalysts for production of isobutene by dehydroisomerisation of n-butane consist of 0.1–1 wt.% Pt, 0.1–1 wt.% In and/or 0.05–1 wt.% Sn, and 0.5–5 wt.% SiO₂ deposited on the surface of a porous granular γ-Al₂O₃ support having specified physical characteristics. The catalysts, used alone or in combination with SiO₂-Al₂O₃ or Boralite B catalysts, give high yields of the product: for example 45–59% conversion with 20–25% selectivity for isobutene.

New Catalysts for Denitration of Vehicle Exhaust
SAKAI CHEMICAL IND. K.K.  *European Appl. 455,491A*
New denitration catalysts consist of 0.1–10 wt.% Pt, Pd, Ru and/or Ag or their oxides supported on TiO₂, or a rare earth metal oxide plus TiO₂, Al₂O₃, ZrO₂ and/or SiO₂ and Pt, Pd, Ru and/or Ag or their oxides. Other forms of the catalyst are based on zeolites or perovskites. The catalysts are used to remove NOₓ from vehicle exhaust gases in the presence of a hydrocarbon reduction agent, and with O₂, avoiding use of NH₃ as a reductant.

Single Step Production of Methyl Isobutyl Ketone
MITSUBISHI KASEI CORP.  *European Appl. 458,216A*
Methyl isobutyl ketone is produced by contacting acetone and H₂ with a catalyst of Pd/C, Pd/Al₂O₃, Pd black or Pd supported on a metal oxide and/or hydroxide treated with an organosilicon compound. Methyl isobutyl ketone is used as an organic solvent, and is produced in good yield.

Palladium-Tellurium Catalyst for Preparation of Dialkoxynbutenes
RHONE-POULENC CHIM.  *European Appl. 462,031A*
A new method for preparation of dialkoxynbutenes is by reaction of 1,3-butadiene with an alcohol in the presence of O₂ and a catalyst consisting of at least one of Pt, Pd or Rh, particularly Pd, and at least one of Te, Se and/or S, preferably Te, optionally combined with Cu, Sb and/or Sn, on a support.

Method for Minimising Emissions from Methane Fuelled Engines
GENERAL MOTORS CORP.  *European Appl. 468,556A*
A method for reducing the exhaust from CH₄ fuelled engines involves controlling the composition of the CH₄ containing fuel-air mixture to within the range 0.99–1.02, and contacting the combustion products in the exhaust gas with a catalyst consisting of 2–3 parts Pt and one part Pd dispersed as fine particles on an Al₂O₃-based carrier. This method minimises emissions of CH₄, hydrocarbons, CO and NOₓ.

Stable Ruthenium Catalyst for Fischer-Tropsch Synthesis
UOP  *U.S. Patent 5,059,574*
A catalyst for Fischer-Tropsch synthesis of C₃+ hydrocarbons from H₂ and CO consists of 0.3–6.0 wt.% Ru present as particles of 40–60 Å and 0.1–5.0 wt.% of a modifier selected from Al, Si, Pb, As and Bi, preferably Si, on an inorganic oxide support, preferably of Al₂O₃ or TiO₂. The catalyst has modified conversion activity for the Fischer-Tropsch synthesis, but good selectivity and stability.

Palladium Catalyst for Methylpyridine Production
STANDARD OIL CO. (OHIO)  *U.S. Patent 5,066,809*
A process for the production of 3-methylpyridine involves contacting 2-methylglutaronitrile with H₂ and a catalyst containing Pd promoted with at least one of Cr, W, Ni, Co and Ge, on a support preferably containing 0–30 wt.% SiO₂ and 100–70 wt.% Al₂O₃. The catalyst gives high yields, for example 78% yield at 100% conversion.

Catalytic Production of Synthesis Gas from Hydrocarbons
EASTMAN KODAK CO.  *U.S. Patent 5,068,057*
Synthesis gas with an H₂:CO molar ratio of 1:1.5–2:1 is produced by contacting an anhydrous mixture of CO₂ and one or more hydrocarbons with a fixed catalyst bed of Pt or Pd on Al₂O₃ or SiO₂-Al₂O₃, at 650–1000°C. The reaction proceeds smoothly with no apparent loss of catalyst activity, and the process gives higher CO:H₂ ratios than conventional steam reforming, so the synthesis gas is suitable for hydroformylation or carbonylation.

Platinum-Gallium Catalyst for Isomerisation of Xylenes
UOP  *U.S. Patent 5,081,084*
A catalyst for isomerisation of alkyl aromatic hydrocarbons consists of a Pt group metal, especially 0.1–1.0 wt.% Pt, optionally 0.05–0.5 wt.% S, a Ga substituted pentasil zeolite containing 0.1–10 wt.% Ga, and an Al₂O₃ matrix. The catalyst is used for isomerisation of xylenes containing ethylbenzene, by contact in the presence of H₂ at 300–500°C and 69–6895 kPa, and gives an optimised yield of para-xylene without the high loss of C₈ aromatics.
Preparation of Biphenyltetra carboxylic Acid in High Yield
DU PONT DE NEMOURS CO. U.S. Patent 5,081,291
3,3',4,4'-Bisbenzoylbenzoic acid is prepared from an alkaline solution of the Na or K salt of 4-bromophthalic acid, at 50-150°C, using hydroxylamine, and in the presence of a 1-10 wt.% Pd/C catalyst. The process uses less than one tenth of the catalyst required in prior art processes, and gives a high yield of the product which is used as a starting material for heat resistant polyimide resins.

Palladium Catalyst for Removal of Nitrogen Oxides from Exhaust Gas
AGENCY OF IND. SCI. TECH. Japanese Appl. 3/221,143
A catalyst for NOx removal consists of Pd supported on an oxide support containing >5 wt.% Mg, for example MgO. The catalyst can decompose NOx into sit, and O3, without using a reducing agent and is used for efficient removal of NOx from combustion exhaust gas from diesel engines and boilers.

Three-Way Catalyst with Separate Rhodium and Platinum Layers
NISSAN MOTOR K.K. Japanese Appl. 3/232,531
A catalyst for purification of internal combustion engine exhaust gas consists of a honeycomb support, a first layer containing Pt and/or Pd, and a second layer containing a mixture of Rh black of <1000 Å particle diameter and a metal oxide—preferably Al2O3, optionally mixed with ZrO2, TiO2 or a rare earth element oxide. The catalyst removes hydrocarbons, CO and NOx from the exhaust gas, and has less deterioration in activity at high temperature by inhibiting formation of a solid solution of Rh and Al2O3.

Palladium Catalyst for Production of Diphénylène Derivatives
MITSUBISHI KASEI CORP. Japanese Appl. 3/232,825
1,2-Diphenyléthylene derivatives are produced by catalytic hydrogenation of benzoyl derivatives such as benzoin or 4,4'-dimethylbenzoin at 0-200°C, in the presence of a Pd catalyst such as 5% Pd/C, 1% Pd/C or 2% Pd/Al2O3, in an organic solvent. The products are produced under mild conditions, at the usual temperature, under atmospheric pressure, and are useful as intermediates for ethanone oximes as anti-ulcer agents.

Ruthenium Catalyst for Coal Liquefaction
AGENCY OF IND. SCI. TECH. Japanese Appl. 3/242,243
Coal liquefaction using H2 gas is carried out in the presence of a solvent and a Ru catalyst. In an example the catalyst was prepared by impregnating FeS2 with Ru trichloride at 120°C, to give a catalyst containing 0.013 wt.% Ru. This method uses a small amount of catalyst, gives improved efficiency of coal liquefaction, and uses moderate reaction conditions.

Aromatic Hydrocarbon Production Using Crystalline Platinum-Gallosilicate Catalyst
NIPPON MINING K.K. Japanese Appl. 3/262,539
Aromatic hydrocarbons are produced from 2-7C aliphatic and/or alicyclic hydrocarbons by contacting with a crystalline gallosilicate catalyst containing Pt. The catalyst is prepared by maintaining a solution of Si, Ga and Pt compounds and an alkali metal salt at a pH of 9-12 and 100-200°C, for 3-200 h. Using the catalyst, higher conversion and selectivity can be obtained.

Combustion Catalyst with Several Catalytic Layers
BABCOCK-HITACHI K.K. Japanese Appl. 3/275,140
A combustion catalyst consists of a support with at least three layers of Pd and/or Pt loaded catalysts placed along the flow direction of the combustion gas. Higher activity can be obtained by replacing part of the Pt catalysts with less expensive Pd catalysts. The combustion catalyst is used to combust methane- or propane-containing fuel in hydrocarbon gas combustors, or to remove CO, hydrocarbons, ethyl acetate or aldehyde from car exhaust.

Palladium Catalyst for Preparation of Unsaturation Dieters
TOSOH CORP. Japanese Appl. 3/275,141 and 3/279,349
A Pd catalyst is used to prepare an unsaturated diester from a conjugated diene, a carboxylic acid, O, and optionally an organic halogen compound, at 140-210°C, under ordinary or elevated pressure. The catalyst contains Pd, Sb, V, a metal carboxylate and a metal halide, and is optionally prepared by treating a silicic acid support and the catalyst metal with tartaric acid and HCl solution, then reducing.

Alloy Catalyst with Varied Uses
YOSHIDA KOGYO K.K. Japanese Appl. 3/275,144
An amorphous alloy containing Zr or Ti; Fe, Co, Cu or Al; and Pd or Pt is thermally treated in an oxidising atmosphere at three temperature steps to form an alloy catalyst, useful for catalytic combustion of H2, reduction of NOx and SOx, or decomposition of fluorocarbons. In an example, a Zr,Co,Pd, amorphous alloy is thermally treated at 250°C for 64 h, 300°C for 170 h, and 700°C for 2 h to form a crystalline alloy catalyst.

Rhodium Catalyst System for Preparation of N,N-Dimethylacetamide
MITSUBISHI GAS CHEM K.K. Japanese Appl. 3/275,656
N,N-Dimethylacetamide is prepared by reaction of trimethylamine with CO in the presence of a catalyst consisting of elemental Rh and elemental I and/or Br, with an at. ratio of I or Br:Rh of 0.1-100. The product is obtained with high selectivity (77.7-89 mol %), at a good reaction rate, under reduced pressure.

Platinum Metals Rev., 1992, 36, (3) 174
HOMOGENEOUS CATALYSIS

Palladium Catalyst System for Thiolester Preparation
SHELL INT. RES. MIJ. B.V. British Appl. 2,246,130A
A thiolester is prepared from an olefinically unsaturated compound, CO and a primary thiol in the presence of a catalyst system consisting of a source of Pd cations, a phosphine having a defined measure of basicity, and a protic acid. Primary thiols have not previously been reactive in this type of reaction, but using this method a good reaction rate and high selectivity to the thiolester are obtained.

High Yield Production of High Purity Aniline
MITSUI TOATSU CHEM. INC. European Appl. 458,006A
Aniline is prepared continuously by hydrogenation of nitrobenzene at 150–250°C under anhydrous conditions, in the presence of a catalyst of Pd or Pd-Pt deposited on a lipophilic C suspended in an aniline solvent, and with a Zn compound and an alkali metal carbonate or bicarbonate as promoters. High purity aniline free of unreacted nitrobenzene is prepared in high yield; and is suitable for methyleneedianiline production without further purification.

Osmium Catalyst for Asymmetric Dihydroxylation of Olefins
MASSACHUSETTS INST. TECH. World Appl. 91/16,322A
An asymmetrically dihydroxylated olefin is prepared by combining a polymeric chiral ligand which is an alkaloid or alkaloid derivative, an organic solvent, an aqueous solution, a base, K ferricyanide, adding a saturated compound, CO and a primary thiol in the presence of Ru and/or Rh halide(s), preferably chlorides, and phosphine(s), for example tributylphosphine or triphenylphosphine.

Preparation of Silylamines with Improved Yield
MITSUI TOATSU CHEM. INC. Japanese Appl. 3/261,789
Silylamines are prepared from the reaction of amines with hydroxilanes at 0–300°C in the gas or liquid phase, in the presence of Ru and/or Rh halide(s), preferably chlorides, and phosphine(s), for example tributylphosphine or triphenylphosphine.

FUEL CELLS

Quaternary Platinum Alloy Electro catalyst for Acid Fuel Cell
N.E. CHEMCAT CORP. European Appl. 469,514A
An electrocatalyst consists of a conductive carrier and a dispersed alloy which is preferably a solid solution having a cubic ordered structure; consisting of 40–70 at.% Pt, 9–27 at.% Co, 9–27 at.% Ni and 9–27 at.% Cu. The electrocatalyst has improved activity and life, and is used in an acid electrolyte fuel cell.

Preparation of High Loading, Noble Metal Alloy Catalysts for Fuel Cells
INT. FUEL CELLS World Appl. 91/19,566A
A noble metal alloy catalyst is prepared by precipitating a noble metal compound from solution onto a support, reducing the activity of the precipitate to prevent re-solution, adding a soluble alloying metal compound to the solution, precipitating onto the support, and calcining at 500°C under H2. The noble metals are preferably Pt and Pd. The method gives high loadings, reduced waste, and is used for fuel cell catalysts.

CORROSION PROTECTION

Corrosion Resistant Stainless Steel Containing Palladium
MITSUBISHI JUKOGYO European Appl. 458,606A
A Pd-containing austenitic stainless steel for use in a highly acidic, high temperature environment contains 0.04–0.04 wt.% C, 5–7 wt.% Si, up to 2.0 wt.% Mn, 15–25 wt.% Cr, 4–24 wt.% Ni, 0.01–1.07 wt.% Pd, balance Fe, <50 ppm O, and unavoidable impurities of P and S. The steel is for use in absorption towers, pumps and vessels in the H2SO4 industry.
ELECTRICAL AND ELECTRONIC ENGINEERING

Magnetic Recording Media Having Vertical Magnetisation Films

OKI ELECTRIC IND. K.K. European Appl. 459,411A and 459,413A

Magnetic recording media consist of a substrate and a vertical magnetisation film, where the latter is either (a) an artificial superlattice of alternate layers of Co and Pt or Pd, or (b) an artificial superlattice of alternate Co and Pt layers, and a Pt, Pd or Co thin film alternately deposited on the substrate. The magnetic recording media have high residual flux density, high coercivity and low Curie temperature.

Magneto-Optical Devices with Laminated Film Containing Platinum

SANYO ELECTRIC K.K. Japanese Appl. 3/224,210

Magneto-optical devices for use in optical isolators, optical shutters or optical memory devices are produced by alternately soaking or contacting a substrate with a solution containing at least a transition metal ion or its reducing agent, and a solution containing at least a Pt ion. The method gives a laminated film of low energy and particle diffusion on the interface.

Magneto-Optical Recording Medium with Improved Rectangular Angle

SUMITOMO METAL IND. K.K. Japanese Appl. 3/230,342

A magneto-optical recording medium that can be over-written consists of a magnetisation film preferably made of Fe, up to 40 at.% Pt, optionally a solid state material excluding Fe and Pt, and unavoidable impurities. The medium has lowered Curie temperature and coefficient of thermal expansion, and lateral Kerr effect.

Conductive Paste Composition for Filling Via Holes

SUN WAVE IND. K.K. Japanese Appl. 3/250,068

A conductive paste composition consists of (a) 80–90 wt.% Pd solder and 10–20 wt.% organic vehicle, or (b) 30–80 wt.% Ni solder, 5–50 wt.% Ag, 5–15 wt.% Co-W carbide and 10–20 wt.% organic vehicle. The composition is useful for electrically bonding conductive materials without the use of lead wire or wire bonding, prevents oxidation, has good adhesion, and is stable up to 850°C.

Electric Switch Contact Element Containing Palladium

SIEMENS A.G. German Appl. 4,013,627

A contact element consists of a non-porous metal support having a 2–6 μm thick Pd-containing deposit, which has an at least 0.1 μm thick Pd-Au or Pd-Ag alloy outer layer with an Au or Ag content of 40–90 wt.%. The contact element is used for an electric switch contact, especially for electromagnetic relays.

Nucleation Process for Partial Currentless Metallisation

ELEKTRONIK-EB-G.m.b.h. East German Patent 292,444

In partial currentless metallisation, the lacquer structure of dielectric or non-catalytically working surfaces is dissolved and nucleation with Pd or Ag atoms with an atom concentration of at least 0.1 mg/dm² is effected. The Pd or Ag atomic structure left on the surface is metallised using chemically reductive baths to give a multi-layer arrangement completely enclosing the contact layer system. The method is used for production of microcircuits for chip structures.

TEMPERATURE MEASUREMENT

Thermocouple Assembly for Metallurgical Vessel

VESUVIUS CRUCIBLE C. U.S. Patent 5,071,258

A thermocouple assembly for sensing the temperature of molten metals in a metallurgical vessel includes a double bore insulator containing the 2 noble metal alloy lead wires of the thermocouple, preferably Pt-Rh alloys. O₂ is able to diffuse along the bores of the double bore insulator to protect the Pt alloy from reaction with C and silica which may be present in trace amounts. The assembly can be used as a tundish in continuous steel casting, and helps to avoid e.m.f. drift.

Temperature Sensor with Platinum Alloy Flange

UCHU KAIHATSU JIGYO Japanese Appl. 3/239,932

A temperature sensor consists of a rod-shaped wound frame having a cap-shaped Pt alloy flange fitted at one end, which is fitted inside a connecting metal fitting, and bonded with a soldering material. The ceramics wound frame can be bonded with the connecting metal fitting, and the difference in elongation created at high temperature can be absorbed by the Pt alloy flange, so that the cable is not broken.

MEDICAL USES

New Platinum Double Nuclear Complexes Useful as Anti-Oncotic Agents

SANKYO K.K. Japanese Appl. 3/271,297

Tetra-co-ordinated divalent Pt double nuclear complexes are new, for example cis-(trans-(1)-1,2-diaminocyclohexane) Pt(II)-N-(cis-diamminehydroxy Pr(II))-azetidine-2-one-4,4-dicarboxylate. The complexes have high anti-oncotic action so are useful as anti-oncotic agents, and have reduced side effects such as nephrotoxicity or marrow depression.

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