

Low-Temperature Sintering of Pd/Ge Films on GaAs

H. R. GRINOLDS and G. Y. ROBINSON, *Appl. Phys. Lett.*, 1979, **34**, (9), 575-577

Rectifying metal-semiconductor contacts, produced by heat treatment of a thin evaporated layer of Pd/Ge on n-type GaAs, were studied by Auger spectroscopy, X-ray diffraction and current-voltage measurements. During sintering at temperatures $< 350^{\circ}\text{C}$, Pd and Ge interdiffused on the non-reacting GaAs substrate forming PdGe and Pd₂Ge. The form of the germanide phases altered the Ge LMM Auger spectra and produced an increase in the Schottky barrier energy from 0.67 to 0.85 eV. In general, sintered contacts have greater planar contact surface than alloy contacts.

Comparative Study of Chemical and Polarization Characteristics of Pd/Si and Pd/SiO_x/Si Schottky-Barrier-Type Devices

L. L. TONGSON, B. E. KNOX, T. E. SULLIVAN and S. J. FONASH, *J. Appl. Phys.*, 1979, **50**, (3), 1535-1537

AES and ISS studies of the chemical nature of semitransparent ($\sim 125\text{\AA}$) Pd/Si Schottky-barrier type devices were performed. Pd silicide was formed in the metal-semiconductor structures, while the presence of an ultrathin ($\sim 30\text{\AA}$) purposely grown semiconductor oxide film inhibited the chemical reaction between Pd and Si in the metal overlayer. Chemical bonding information was correlated with barrier height.

MEDICAL USES

cis-Platinum: A New Anticancer Agent

C. J. WILLIAMS and J. M. A. WHITEHOUSE, *Br. Med. J.*, 1979, **1**, 1689-1691

A review of the drug platinum diamminodichloride (cisplatin) is presented, aimed at providing clinicians with information on the optimal methods of use, the toxicity and the anti-tumour effects of the drug.

Co-ordinate Compounds with Potential Anti-Tumour Activity. I. Platinum and Palladium Complexes with Aminic Ligands

S. KIRCHNER, C. DRĂGULESCU, A. MAURER, V. TOPCIU and N. CSAKI, *Rev. Chim.*, 1979, **30**, (4), 321-326

A number of complexes of Pt(II) and Pd(II) of the *cis*-dichlorodiammine type with hydrazine and organic cyclic saturated amines have been prepared, characterised and tested in vitro and in vivo for their anti-tumour activity. Two of the complexes, one of Pt(II) and one of Pd(II), tested on *E. coli* B rods, led to deformed cells like methotrexate and exhibited quite good anti-tumour activity against Ehrlich ascites in a preliminary stage, but were almost inactive against advanced Ehrlich ascites.

Synthesis and Antimitogenic Activity of Some Co-ordination Compounds of Platinum(II), Palladium(II) and Rhodium(III)

A. VASSILIAN, A. B. BIKHAZI and H. A. TAYIM, *J. Inorg. Nucl. Chem.*, 1979, **41**, (5), 775-778

Complexes of Pt(II), Pd(II) and Rh(III) with 2,6-dimino-pyridine and its 4-methoxy and 4-ethoxy derivatives were prepared and their antimitogenic activity was measured. Pt(II) complexes showed high antimitogenic activity and low toxicity. Pt(II) complexes were moderately active, while Rh(III) complexes enhanced thymidine uptake. The behaviour of Rh(III) complexes was of particular interest because such complexes may exhibit anti-tumour activity by enhancing the immune response of the system.

Age Hardening of Ag-Pd-Cu Dental Alloy

M. OHTA, K. HISATSUNE and M. YAMANE, *J. Less-Common Metals*, 1979, **65**, (1), P11-P21

The age-hardening characteristics of Au containing Ag-Pd-Cu dental alloys were investigated. Compositions examined were Ag 49.3-52.5 at.%, Pd 24.5-29.3 at.%, Cu 15.3-21.0 and Au 2.6-6.5 at.%. Hardening was found to be due to the precipitation of a CuPd ordered phase, with a AuCu-I type face centred tetragonal structure.

NEW PATENTS

METALS AND ALLOYS

Nickel-Palladium Brazing Alloy

WESTERN GOLD & PLATINUM CO.

U.S. Patent 4,149,881

A brazing alloy which can be used as a cheaper alternative to 82Au-18Ni alloys contains 17-44% (36%) Pd, 4-11% (11%) Cr, 1-4% (2.2%) Si, 1.5-4% (2.1%) B and the balance (48.7%) Ni, and has a brazing temperature of about 1800°F. The preferred composition is given in brackets.

ELECTROCHEMISTRY

Electrode for Electrolytic Cell

ESB INTERNATIONAL CORP.

British Appl. 2,009,491 A

A composite electrode, particularly for use in lead-acid batteries, has a porous body of Ti infiltrated with a metal and an outer layer of an electroconductive metal oxide to prevent electrolyte access to the electrode interior. The pores can be filled with Ru, Pb, Sn, Sb or Mn.

Long-Life Brine Electrolysis Electrodes

HOECHST A.G.

U.S. Patent 4,140,813

The electrodes are prepared by flame or plasma spraying Ti oxide on to an inert substrate (such as Ti or a Ti alloy) and thermally decomposing a compound to deposit platinum group metal or metal oxide (such as Ru and/or IrO₂) on to the rutile Ti oxide coating.

Photolysis of Water

E. I. DU PONT DE NEMOURS & CO.

U.S. Patent 4,144,147

Rhodate p-type semiconductors (rho-Rh₂O₃, rho-LuRhO₃, rho-LaRhO₃ and rho-DyRhO₃) are used as stable cathodes in a photolysis cell for decomposing water into H₂ and O₂ by sunlight.

Oxidation Electrodes

SIEMENS A.G.

German Offen. 2,727,852

Electrodes for the electrochemical oxidation of alcohol, for instance in fuel cells, are of porous Ni impregnated with a mixture of Pt, Pd and Bi.

ELECTRODEPOSITION AND SURFACE COATINGS

Intermetallic Cladding of Superalloys

JOHNSON MATTHEY & CO. LTD.

British Appl. 2,005,729 A

Metallic substrates, particularly turbine blades, are coated with an intermetallic compound having the formula A_xB_y, where A is Be, Al, Sc, Y, a lanthanide metal, Si, Ti, Zr, Hf, Th, V, Nb or Ta; B is Pt, Pd, Rh, Ir or Ru and x and y are integers between 1 and 5. The coatings are applied by pack diffusion, chemical vapour deposition, sputtering, electroless deposition, or by electrolysis. The thickness of the coating is preferably between 2 and 15 microns.

LABORATORY APPARATUS AND TECHNIQUE

Solid Electrolyte Oxygen Sensor

WESTINGHOUSE ELECTRIC CORP.

U.S. Patent 4,134,818

A sensor consists of a high temperature solid electrolyte electrolytic cell, and a temperature sensor for monitoring temperature changes resulting from catalytic combustion at the cell electrodes. The electrodes are preferably of Pt, but can also be of Pd or Ru.

Photoelectric Apparatus for Water Splitting

PURDUE RESEARCH FOUNDATION

U.S. Patent 4,140,591

The efficiency of a photoelectric cell, for H₂ production, having a substrate carrying a Pt black layer and an upper layer of chlorophyll and dihydrate polycrystals, is increased by depositing a second layer of Pt black on top of the chlorophyll dihydrate layer.

Oxygen Cell

J. POTTSCHKE

German Offen. 2,749,357

A cell for measuring the dissolved O₂ in molten metals has a solid electrolyte of Cr oxide mixed with Y oxide-stabilised ZrO₂, an external electrode, and an internal electrode which is of Mo or a high-melting Pt-Rh alloy.

JOINING

Thermoplastic Braze Paste

JOHNSON MATTHEY & CO. LTD.

British Appl. 2,004,489 A

The storage life and application properties of brazing alloy pastes is improved if the brazing alloy powder is mixed with a thermoplastic material (such as a resin-wax mixture). The composition can also optionally contain flux. The addition of a thermosetting material, such as a phenol- or urea-formaldehyde resin, improves adhesion of the brazing paste to the joint. Conventional Pd, Au and Ag brazing alloy compositions are used in the pastes.

HETEROGENEOUS CATALYSIS

Foamable Siloxanes

DOW CORNING CORP.

British Patent 1,543,215

Non-toxic, fire retardant foams are prepared from organo-hydrogen siloxanes containing alkyl, phenyl or 3, 3, 3-trifluoropropyl radicals and a Rh complex catalyst.

Methane Preparation

TEXACO DEVELOPMENT CORP.

British Patent 1,544,730

Methane can be prepared by the selective conversion of hydrocarbons (heptane, hexane, butane, benzene or methylcyclo-propane) using, as the catalyst, a finely divided high surface area substrate impregnated with 0.01–99.99% of a platinum group metal and 99.99–0.01% of an iron group metal, preferably Fe, Co or Ni.

Multimetallic Catalytic Composite

U.O.P. INC.

British Appl. 2,004,764 A

Superactive catalysts for use in hydrogenation—dehydrogenation reactions are formed from a pyrolysed Re carbonyl component and a platinum group metal-impregnated porous carrier which preferably also contains a halogen component. Other metal components, including Ag, Au and the lanthanide metals, can be incorporated into the carrier.

Electric Cells

UNITED KINGDOM ATOMIC ENERGY AUTHORITY

British Appl. 2,006,514 A

Contaminants in an electrolyte are catalytically converted to an acceptable form. In a Ni oxide-H₂ cell, dissolved O₂ is catalytically converted to water or hydroxyl ions by means of a Pt screen.

Catalytic Oxidation of Ammonia

JOHNSON MATTHEY & CO. LTD.

British Appl. 2,009,120 A

Ammonia can be oxidised by passing it, mixed with air, through catalyst particles at a flowrate which forms the particles into a fluid bed. Platinum group metal catalysts, particularly Pt-containing intermetallics, for instance Pt₃Zr, are preferred catalysts. The NH₃ oxidation process is used for HNO₃ production.

Removing Oxygen and Water Impurities from Hydrogen

BILLINGS ENERGY CORP. *British Appl.* 2,011,365 A

O₂ and water impurities are removed from H₂, which is to be stored in tanks containing hydride-forming alloys, by passing the gas through a catalyst bed, for instance containing a platinum group metal or a lanthanide in combination with other catalytic metals (where O₂ and H₂ are converted to water) and then adsorbing water from the gas stream. Upon release of the H₂ from the hydride forming metal alloy, it passes back through the adsorbent, thereby cleansing the adsorbent of water impurities.

Metal Fluorides and Oxyfluorides

EXXON RESEARCH & ENGINEERING CO.

British Appl. 2,012,256 A

Metal fluorides and oxyfluorides for catalytic and other uses are produced by reacting a metal oxide with a fluorohydrocarbon. The metals listed include Rh, Ir, Os, Ru, Ag, Eu, Lu, Nd and La.

Hydrocarbon Dehydrogenation Catalyst

U.O.P. INC.

U.S. Patent 4,131,628

Greater catalyst selectivity can be obtained using a non-acidic composition containing 0.01–2% platinum metal (Pt), 0.01–2% Re, 0.05–5% Co, 0.01–5% Sn and 0.1–5% Group IA or IIA metal supported on a porous carrier. The Pt, Re, Co are present in the elemental state under dehydrogenation conditions and the Sn as an oxide and the average crystallite size of the Re and Co is less than 100Å.

Methanation Catalyst

AMERICAN GAS ASSOCIATION *U.S. Patent* 4,132,672

The activity and S-resistance of supported Ni catalysts, used in methanation processes, is increased when a small amount (0.1–1.0%) of Ir is incorporated in the catalyst.

Platinum Catalyst

UNITED TECHNOLOGIES CORP.

U.S. Patent 4,137,373

The rate of Pt recrystallisation of Pt-C catalysts used in phosphoric acid electrolyte fuel cells is reduced and its activity increased by depositing porous C on and around the crystallites and then heating the catalyst in an inert atmosphere or vacuum at a high temperature.

Isomerisation Process

RHONE-POULENC S.A.

U.S. Patent 4,138,411

Aromatic alkenyl compound isomerisation, particularly of eugenol and safrole to isoeugenol and isosafrole, is carried out with an Os or Ru catalyst.

Hydrogenation of Naphthene Hydrocarbons

U.O.P. INC.

U.S. Patent 4,139,570

Non-acidic catalysts for the dehydrogenation of naphthene hydrocarbons contain 0.01–2% of a platinum group metal (Pt), 0.05–5% Co and 0.01–5% Bi on a porous carrier.

Increasing the Isobutane Content of a Hydrocarbon Cut

INSTITUT FRANCAIS DU PETROLE

U.S. Patent 4,140,621

An olefinic 4C cut containing both butane and isobutane is subjected to selective hydrogenolysis in the presence of a Rh catalyst supported on a specific Al₂O₃ carrier so that the butane is selectively converted to ethane and propane, while isobutane is preserved or is formed.

Hydrocarbon Conversion Catalyst

EXXON RESEARCH & ENGINEERING CO.

U.S. Patent 4,141,817

Stable catalysts for use in high temperature oxidation applications consist of a Group VIII metal, preferably Ir, in combination with a Group IIA metal oxide (Ca, Ba or Sr oxide) supported on a non-acidic refractory oxide support.

Transition Metal Catalysts

RESEARCH COUNCIL OF ALBERTA

U.S. Patent 4,142,993

NH₃ synthesis catalysts are prepared by doping an activated C support with a series of solutions. These solutions contain a Group IIA metal, a Group VIII metal, preferably Ru, a Group IA metal and optionally a lanthanide metal and/or a Group IIIA metal salt. Preferred catalysts contain Ru, Ba, La and K.

Mo and W Bronzes for NO_x Decomposition

JOHNSON MATTHEY & CO. LTD.

U.S. Patent 4,143,120

A NO_x reduction catalyst, for use with CO and hydrocarbon containing gas and air streams, is formed from a mixture of Pt and a bronze having the formula H_xWO_y, where x is less than 0.5 and y is between 2 and 3. A preferred bronze has the formula H_{0.16}WO_{2.6}. The body of the specification discloses the use of a wider range of bronzes having the formulae A_xBO_y and C_xD₃O₄, where A is Group IA, IIA and lanthanide metals, Ba, Pb, Tl, Ni, Cu, NH₄, Ag and H, B is Pt, Ti, V, Nb, Mo, Ta, W or Re, C is Na, Mg, Ni, Ca, Cd or Sr and D is Pd or Pt and x is between 0 and 2 and y between 2 and 3, not necessarily in admixture with Pt.

Rhodium-Cobalt Carbonyl Cluster Hydroformylation Catalysts

DOW CHEMICAL CO. *U.S. Patent 4,144,191*
Rh-Co carbonyl bimetallic cluster catalysts loaded on to an amine resin support are highly selective catalysts for converting olefins to alcohols using a one step oxo-hydroformylation process. A preferred bimetallic cluster has the formula $Rh_xCo_yCO_{12}$, where x and y are integers 1-3.

Platinum Group Metal Catalysts

EXXON RESEARCH & ENGINEERING CO.
U.S. Patent 4,145,314

Highly dispersed platinum group metal catalysts are prepared by the redispersion of sintered or agglomerated supported Group VIII-P intermediate catalytic materials, by heat treatment in an inert atmosphere at a temperature preferably between 630 and 700°C, followed by decomposition of the compounds by heat treatment in air.

Shutdown Operation of a Catalytic Cracker

MOBIL OIL CORP. *U.S. Patent 4,146,464*
A platinum group metal or Re combustion promoter is introduced into the circulating inventory of catalyst in a cracking process to temporarily change the operating mode of the generator and reduce the CO content of the flue gas, thus permitting temporary shutdown of the CO boiler and CO incinerator, while continuing the catalytic cracking process.

Acidic Multimetallic Catalyst for Hydrocarbon Conversion

U.O.P. INC. *U.S. Patent 4,149,961*
Acidic catalysts particularly suitable for increasing the octane rating of petroleum contain 0.01-2% Pt or Pd, 0.01-2% Rh, 0.01-1.0% In and 0.1-3.5% of a halogen. The noble metals are present as metals and the In in an oxidation state above that of the elemental metal.

Silylhydrocarbyl Phosphine Transition Metal Complex Catalysts

EXXON RESEARCH & ENGINEERING CO.
U.S. Patent 4,151,114

A novel method of anchoring transition metal phosphine complexes (such as Rh and Ni complexes) to SiO_2 bases is described in which a reactive silane group and the complex-forming phosphine group are chemically linked via a divalent hydrocarbon radical. The bridged sila-phosphines are then anchored and complexed with the transition metal.

Catalytic Conversion of Organic Chlorine Compounds

BAYER A.G. *U.S. Patent 4,151,262*
A two-stage oxidation process for converting organic chlorine compounds into CO_2 and HCl uses a Pt catalyst in the first zone and a Pd catalyst in the second zone.

HOMOGENEOUS CATALYSIS

Dihydroxy Phospholane Oxides

BAYER A.G. *British Patent 1,548,317*
3,4-Dihydroxyphospholane oxides, used as catalysts for the conversion of isocyanates to carbodiimides, are prepared by reacting phospholene oxide derivatives with H_2O_2 in the presence of Os compounds as catalyst. K osmate and OsO_4 are used in the examples.

Catalyst for Polyhydric Alcohol Synthesis

UNION CARBIDE CORP. *British Appl. 2,004,867 A*
A novel Rh carbonyl carbide cluster compound is particularly effective for the production of ethylene glycol from synthesis gas when used in association with certain alkali metal cations. A preferred cluster catalyst has the formula $Cs_2(Rh_6(CO)_{13}C)$.

Catalyst for Polyhydric Alcohol Production

UNION CARBIDE CORP. *British Appl. 2,006,202 A*
Rh carbonyl sulphur catalysts show good stability when used for the production of ethylene glycol from mixtures of H_2 and C oxides.

Ruthenium Promoter for Ethanol Production

GULF RESEARCH & DEVELOPMENT CO.
U.S. Patent 4,133,966

In the selective formation of ethanol from methanol, H_2 and CO in the presence of a catalyst system containing cobalt acetylacetonate and a Group VA tertiary organic compound, I and a Ru compound are used as promoters.

Manufacture of Vinyl Acetic Acid

HOECHST A.G. *U.S. Patent 4,140,865*
Vinyl acetic acid and optionally gamma-butyrolactone are prepared economically, in good yield, by reacting oxygen-containing allyl compounds (allyl acetate, propionate and isobutyrate) with CO in the presence of a heavy metal catalyst, preferably $RhCl_3 \cdot 11_2O$, $Ni(CO)_4$ and PdI_2 .

Exchange Resin-Metal Complex Catalyst

MOBIL OIL CORP. *U.S. Patent 4,145,486*
Complexes formed by contacting a weak base anion exchange resin with a solution of coordination compound having two ligands connected to one central metal atom, to replace one ligand with the resin, are effective catalysts for hydrogenation, polymerisation, etc. Preferred metal complexes contain Pt, Pd, Rh, Sn and Ni.

Rhodium Oxidation Catalyst

INSTITUT FRANCAIS DU PETROLE
French Appl. 2,395,244
Unsaturated ethers are prepared by the oxidation of olefins in the presence of an alcohol using as catalyst a combination of ML_mX_n

and $M'L'_qZ_p$ where M is Rh, M' is Fe, Cu, Co or Ni, X and Z are anionic groups, L and L' are each water or an organic ligand, such as an olefin, n is 1-3, m is 1-3 or 6, or is 0, p is 1-3 and q is 0 or 1-6.

FUEL CELLS

Fuel Cells

UNITED TECHNOLOGIES CORP.

British Appl. 2,011,155 A

A regenerative fuel cell operated with H_2 and Cl_2 uses an anhydrous electrolyte or a molten salt having a low vapour pressure, to avoid corrosive action of the Cl_2 . Hydrogen electrodes used in the cell are coated with a catalyst layer which is preferably Pt, and chlorine electrodes are coated with a catalyst layer which is preferably RuO_2 .

Fuel Cell Electrode

U.S. SECRETARY OF THE ARMY *U.S. Patent 4,141,801*

A fuel cell anode for use in methanol-air and ethylene glycol-air fuel cells, having reduced catalyst loading, is prepared by pressing a paste mix containing a platinum group metal (Pt or Pd) powder, graphite and Teflon on to a collector grid, drying and cathodically charging the anode using a saturated Pb chloride electrolyte to deposit Pb, and then anodically charging to convert the Pb coating to Pb oxide.

GLASS TECHNOLOGY

Glass Fibre Production

KAISER GLASS FIBER CORP. *British Patent 1,546,204*

In a plant for glass-fibre production, the flow channel is lined with Pt foil, and the orifice plate is of 90% Pt-10% Rh alloy.

ELECTRICAL AND ELECTRONIC ENGINEERING

Intermetallic Electrode Materials

JOHNSON MATTHEY & CO. LTD.

British Appl. 2,005,649 A

Igniter electrodes for use in I.C.E., gas turbines and jet engines, having improved erosion resistance, have working surfaces formed from an intermetallic compound of general formula A_xB_y , where A is Be, Al, Sc, Y, a lanthanide metal, Si, Ti, Zr, Hf, Th, V, Nb or Ta, B is Pt, Pd, Rh, Ir or Ru, and x and y are between 1 and 5. Ta-Rh, Ta-Ir, Nb-Rh and Nb-Ir are preferred combinations, being unusually ductile.

Pressure Sensitive Resistance Elements

SHIN-ETSU POLYMER CO. LTD.

U.S. Patent 4,145,317

Pressure sensitive resistance elements are prepared from a rubbery elastomer matrix having conductive particles (Pt, Au, Ag, Fe, Cu, Cr,

etc.) distributed throughout the matrix in a graduated manner. The materials are prepared by allowing evenly distributed particles to settle while the elastomer is cured.

TEMPERATURE MEASUREMENT

Resistance Thermometers

JOHNSON MATTHEY & CO. LTD.

British Patent 1,546,091

A temperature sensitive element as described in *British Patent 1,415,644* is used on a hollow tubular or solid cylindrical substrate in the form of a conducting tortile path to form a resistance thermometer. The resistive material, consisting of a fused vitreous material loaded with electrically conducting particles, preferably Pt particles, is screen printed on to the substrate.

Reduction Resistant Glazes

JOHNSON MATTHEY & CO. LTD.

British Appl. 2,006,521 A

Known high temperature resistance thermometers tend to lose their accuracy when encased in a stainless steel tube. This defect is now avoided by using a vitreous phase resistant to chemical reduction to bind noble metal conductive particles in paths on an Al_2O_3 substrate. If the conductive paths are covered with a glaze this also must be chemically resistant to reductive gases.

MEDICAL USES

Reduced Gold Dental Alloy

JOHNSON MATTHEY & CO. LTD.

British Patent 1,545,054

Dental alloys for restorative applications contain, by weight: Au 25-42%, Ag 5-22%, Pd 45-62%, Ga up to 5%, In up to 2%, and Sn 0-1%. A preferred alloy contains Au 34%, Ag 10%, Pd 50%, Ga 3.72%, In 1.5% and Sn 0.78%.

Cycloalkylamine Complexes of Pt(IV)

JOHNSON MATTHEY & CO. LTD.

British Appl. 2,006,213 A

New agents for the treatment of malignant growths have the composition *trans-Z₂ cis A₂PtXY* in which the A groups are the same or different alicyclic amines, X and Y are halogenoid and the Z groups are OH or halogenoid.

4-Carboxyphthalato-(1,2 diamino-cyclohexane)-Platinum (II)

U.S. DEPARTMENT OF HEALTH, EDUCATION AND

WELFARE

U.S. Patent 4,137,248

Anti-leukemic 4-carboxyphthalato-(1,2 diamino-cyclohexane)-Pt(II) is prepared by reacting dichloro-(1,2 diamino-cyclohexane)-Pt(II) with $AgNO_3$ to replace chloro with nitro.