

ELECTRICAL AND ELECTRONIC ENGINEERING

Control of Palladium Adherence to Silicon Dioxide for Photolithographic Etching

M. S. SHIVARAMAN and C. M. SVENSSON, *J. Electrochem. Soc.*, 1976, **123**, (8), 1258

A method for increasing the adherence of thin Pd film (100 nm) evaporated on to SiO₂ wafer was developed. It consists of annealing the composite in air at 200°C for 30 min, applying a photoresist, spinning, drying, exposure, developing and baking followed by etching with 1:10:10 HCl:HNO₃:CH₃COOH and resist removal in acetone. The air annealing at 200°C is assumed to extract H₂ from the Pd-SiO₂ surface thus increasing the adhesion of the film.

TEMPERATURE MEASUREMENT

The Melting Temperature of Platinum Measured from Continually Melting and Freezing Ribbons

J. BEZEMER and R. T. JONGERIUS, *Physica B+C*, **83**, (3), 338-346

The melting temperature of Pt was measured by using pure Pt ribbons, 2 mm wide and 0.02 mm thick, heated by a modulated direct electric current to the melting point. The melting of a small centre dot of the ribbon during a fraction of the period causes a rise in emissivity of the centre.

NEW PATENTS

METALS AND ALLOYS

Ruthenium Powder Metal Alloy

GENERAL MOTORS CORP. *U.S. Patent* 3,957,451
A sintered powder metal alloy contains about 75-85% Ru dispersed in a matrix of 15-25% of a pre-alloyed composition consisting of 65-80% Ni, 5-10% Cr, 5-15% W, 4-6% Si and 2-6% Fe. The surface of the Ru powder is soluble in the pre-alloyed composition for ductility and has good oxidation and spark erosion resistance at temperatures as high as ~2000°F. The alloys are used for electrical contacts and sparking electrodes.

Modified Iridium-Tungsten Alloy

U.S. ENERGY RESEARCH & DEVELOPMENT ADMINISTRATION *U.S. Patent* 3,970,450
An Ir base alloy composition having enhanced impact resistance consists of 20-50 p.p.m. Al,

The results showed that the radiance temperature at which the melting starts can be measured with a sensitivity of 0.02K. Pt ribbons with a temperature stabilisation can be therefore used for temperature calibration.

Problems in the Measurement of Temperature with Pt-Rh Thermocouples

L. FROSCHAUER and H. SCHMIDT, *Keram. Z.*, 1976, **28**, (7), 346-348

Temperature measurements made with Pt-Rh thermocouples were found to differ depending on the kind of ceramic sheathing used. The changes of e.m.f. observed at above 1300°C in both oxidising and reducing atmospheres were attributed to Fe or Si impurities in the protective ceramic. The use of Al sheaths with 99.7% Al₂O₃ was recommended.

MEDICAL USES

Complexation of Tetra-μ-carboxylato-dirhodium(II) with Imidazole

K. DAS and J. L. BEAR, *Inorg. Chem.*, 1976, **15**, (9), 2093-2095

The formation constants, the enthalpies and entropies of reactions for the formation of 1:1 and 1:2 adducts of Rh₂(O₂CR)₄ where R = CH₃OCH₂, CH₃ or CH₃CH₂ with imidazole were determined. The order of stability was found to be propionate > acetate > methoxyacetate. The Rh(II) carboxylates were found to have high anti-tumour activity.

20-100 p.p.m. Fe, 5-20 p.p.m. Ni, 50-100 p.p.m. Rh, 15-50 p.p.m. Th and Ir as the balance.

Palladium-Silver Alloy for Use in Nuclear Reactors

COMMISSARIAT A L'ENERGIE ATOMIQUE

French Appl. 2,285,172

For the introduction of gaseous H₂ into H₂O, such as for the hydrogenation of pressurised H₂O in a nuclear reactor, a helicoidal tube of a 77% Pd-23% Ag alloy is employed.

CHEMICAL COMPOUNDS

Intermetallic Ferromagnetic Compounds

INTERNATIONAL BUSINESS MACHINES CORP.

British Patent 1,450,889

The compounds have the general formula R₂TX where R is Rh or Ru, T is Fe, Co, Ni, V, Cr or Cu and X is Al, Ga, In, Tl, Ge, Sn or Sb.

Ruthenium-Containing Developers for Photography

EASTMAN KODAK CO. *U.S. Patent 3,964,912*
A Ru divalent or trivalent cationic complex, such as a hexammine, ethylenediamine or bipyridine complex, is used to accelerate photographic development.

ELECTROCHEMISTRY

Bipolar Electrodes

HOOKER CHEMICALS & PLASTICS CORP.
British Patent 1,446,797

The electrode consists of a layer of a valve metal, a layer of Cu on the cathodic side of the valve metal, and a conductive layer of a Pt group metal or metal oxide on at least part of the anodic side. The layer of Cu is covered.

Electrochemical Cells

SECRETARY OF STATE FOR TRADE AND INDUSTRY
British Patent 1,447,363

A polarographic or coulometric cell consists of a solid body of material surrounding a Pt conductive filament, and has a Au-Ag counter electrode.

Electrochemical Anode

HOOKER CHEMICALS & PLASTICS CORP.
U.S. Patent 3,956,083

Brine electrolysis and other processes may be carried out using an anode having a valve metal substrate coated with a SnO layer doped with Te and with an outer layer of a Pt group metal or oxide, such as RuO₂.

Electrodes Having Silicide Surface

P.P.G. INDUSTRIES INC. *U.S. Patent 3,963,593*
In a brine electrolysis cell the anode is improved by providing a surface of an electroconductive, electrocatalytic silicide chosen from silicides of the Pt group metals on a valve metal substrate. Pt₃Si is the preferred silicide.

ELECTRODEPOSITION AND SURFACE COATINGS

Silicon Metal Joints

P.P.G. INDUSTRIES INC. *U.S. Patent 3,956,098*
A Si fabrication consists of a Si member, an electrodeposited coating of Pd, Pt, Cu, Ni, Sn, Al, Zn, Ag, or Au and a second metallic member bonded to the Si member by an electrically conductive epoxy resin bonding material bonded to the electrodeposited coating.

Electroplating Polyoxymethylene

E. I. DU PONT DE NEMOURS & CO.
U.S. Patent 3,963,590
Polyoxymethylene may be treated with quinoline or butyrolactone before etching and Pd sensitisation to improve the adherence of the subsequent metal coatings.

Osmium or Rhenium Coated Cutting Wire

LUMALAMPAN AB SWEDEN *French Appl. 2,284,403*
A cutting or sawing wire is coated by various substances, including Os or Re in the form of crystals, obtained from a gaseous phase reaction.

Palladium-Nickel Alloy Plating

SCHERING A.G. *German Offen. 2,506,467*
Ni and Pd may be electrodeposited together from an aqueous ammoniacal bath containing the metals in complex form, particularly with amino acids, keto acids, amines and the like. Glycine and alanine are suitable compounds.

LABORATORY APPARATUS AND TECHNIQUE

Determination of Total Oxygen Demand

TORAY INDUSTRIES INC. *British Patent 1,446,827*
A process for determination of total O₂ demand, for example in pollution control of H₂O, uses a combustion chamber with a combustion-supporting catalyst bed. Pt, Pd or Rh form the active catalyst material.

Flame Ionisation Detector

PYE LTD. *British Patent 1,451,795*
The detector has a burner head metallised with a Pt-based alloy in particular areas to provide electrical connection between the burner and external circuitry.

Electrolytic Cell Gas Sensor

CHEN-YEN CHOU ET AL. *U.S. Patent 3,955,268*
A solid state electrolytic cell gas sensor head is made from a mixture of transition metal and non-metallic oxides with a small amount of Pt group metal oxide added. This mixture is formed into a paste and coated on a collector wire and a heater wire to form a bead. For example 2% Pt oxide may be added to an Al₂O₃-SiO₂ mixture.

Selective Metallisation of a Cathode Ray Tube

N.V. PHILIPS GLOEILAMPENFABRIEKEN
Dutch Appl. 75.00616

A photoresist technique is used to produce a mask on a phosphor layer which is then used for sensitising with Pd, Pt, Au, Ag or Cu ions before chemically plating with Ni, Ag, Co, Sn, Cu or Au.

HETEROGENEOUS CATALYSIS

Benzazepine Derivatives

ENDO LABORATORIES INC. *British Patent 1,449,331*
New benzazepine derivatives including (*cis*-2,3-dimethylcyclopropyl)-methyl can be made by catalytic hydrogenation using 5% Pd on charcoal of a corresponding compound including (2,3-dimethylcycloprop-2-en-1-yl) methyl.

Production of Purified Water

CANADIAN PATENTS AND DEVELOPMENTS LTD.

British Patent 1,451,471

Distilled H₂O is vaporised and the vapour passed with a stream of pure O₂ over a catalyst consisting of at least one of Pd, Rh, Ru, Pt, Ir, Fe, Co, or Ni, at 600–900°C. The vapour is then condensed and the steps are repeated until the degree of purity required is obtained.

Method for Making Bimetallic Catalysts

EXXON RESEARCH & ENGINEERING CO.

U.S. Patent 3,956,191

Bimetallic catalysts are prepared by contacting a catalyst consisting of Ag metal in the form of a powder having a surface area of 0.01–1.0 m²/g as such or present on a refractory metal oxide support with an aqueous solution consisting of a salt of a second metal: Pt, Ir or Au. The catalyst has surface alloys or multimetal clusters of the two metals, and it is used in fuel cell electrodes, petroleum processing, etc.

Honeycomb Structure for Countercurrent Gas Flow

W. R. GRACE & CO.

U.S. Patent 3,960,510

A two-stage catalytic reactor for the exhaust system of an internal combustion engine consists of concentric tubes of porous ceramic, coated with Ni oxide and a Pt group metal.

Reductive Alkylation of Ammonia

MERCK & CO. INC.

U.S. Patent 3,962,338

The reductive alkylation of NH₃, a primary amine or a secondary amine, where the amine substituents are straight or branched chain lower alkyl groups, optionally hydroxy substituted, takes place by the dropwise addition of a glycer-aldehyde using a Pt, Pd or Raney Ni catalyst to provide a S-1,2-dihydroxy-3-aminopropane.

Catalyst Manufacture

UNIVERSAL OIL PRODUCTS CO.

U.S. Patent 3,963,643

A catalyst with 0.1–5% Pt group metal on Al₂O₃ is reacted with a Friedel Crafts metal halide in an amount sufficient to introduce from about 2–15% combined halogen into the composite. Then the composite is contacted at a temperature of 100–600°C in a non-reducing atmosphere with a polyhalogen compound containing at least 2 Cl atoms. The product is an improved hydro-conversion catalyst.

NO_x Reduction and Catalyst

JOHNSON MATTHEY & CO. LTD.

U.S. Patent 3,963,827

A process for the reduction of an oxide of N₂ typically present in an automobile exhaust uses a supported catalyst consisting of an inert material impregnated or coated with a mixture or alloy consisting of 5–75% Ru, up to 30% selected base

metal, the lanthanides and the actinides and the balance, ≥5%, Pt. The catalyst may also be used in some oxidation reactions.

Ruthenium Catalyst for Exhaust Gas Purification

JOHNSON MATTHEY & CO. LTD.

U.S. Patent 3,972,837

The catalyst for use in the reduction of pollution from car exhaust gases is made up of a ceramic honeycomb having layers of a catalytically active refractory metal oxide and a catalytic layer comprising a mixture of Pt and one or more compounds selected from the group consisting of CaRuO₃, MgRuO₃, BaRuO₃, SrRuO₃ and a mixture of MgO and RuO₂.

HOMOGENEOUS CATALYSIS

Rhodium Hydroformylation Catalyst

PHILLIPS PETROLEUM CO. *U.S. Patent 3,956,177*

New catalysts are obtained by the reaction of L_nRhX_m, where X is Br, Cl or I, L is a cyclic diene or triene, n is 1 or 2, m is 1 or 2 and n+m is 2 or 3, a hydrazine or Group IA, IIA or IIIA metal and a phosphine or phosphite. In an example the conversion of hexene to mainly heptaldehyde is catalysed by the reaction product of cyclododecadiene Rh dichloride, Na hydride and trinaphthyl phosphite in THF.

Coating Process

DOW CORNING LTD.

U.S. Patent 3,960,810

Siloxane compositions containing components with Si-vinyl and Si-H groups are cured using Rh halide complexes with carbonyl or mercaptan ligands, for example, a methyl hydrogen siloxane-methyl vinyl siloxane mixture was catalysed by the addition of a 3% solution in toluene of RhCl₃(Bu₂S)₃ to provide 40 p.p.m. Rh, of total composition.

CHEMICAL TECHNOLOGY

Separation and Purification of Platinum, Rhodium and Iridium

MATTHEY RUSTENBURG REFINERS (PROPRIETARY) LTD.

U.S. Patent 3,960,549

A solution containing Ir, Rh and Pt is reduced to convert Ir(IV) to Ir(III). The Pt is then extracted with a secondary amine or quaternary ammonium halide or hydroxide. The Ir(III) is reoxidised to Ir(IV) and this may be extracted with secondary amine or quaternary ammonium compound.

Separation of Palladium from Other Platinum Metals

MATTHEY RUSTENBURG REFINERS (PROPRIETARY) LTD.

U.S. Patent 3,967,956

Pd which is present in a solution with at least one other Pt group metal is separated and purified by

adjusting, as necessary, the pH of the solution to make it acidic, contacting the acidic solution with an oxime solvent and separating the organic phase containing substantially all of the Pd present in association with the oxime solvent.

GLASS TECHNOLOGY

Manufacturing Laser Glass

GENERAL ELECTRIC CO. *British Patent 1,449,215*
Laser glass is made in a vessel formed of or having a lining of Pt or an alloy consisting of at least 90% Pt and $\leq 10\%$ Ru or Au. He gas is bubbled through the melt for sufficient time to remove any bubbles of gas formed during the batch reaction, and the melt is refined in the presence of a dry gas stream consisting of one or more of Ne, Ar, etc.

Stirring of Molten Glass

PILKINGTON BROTHERS LTD. *U.S. Patent 3,971,646*
A stirrer for stirring molten glass consists of a stirring member for immersion in the molten glass and a driven rotary shaft extending upwards from the stirring member to a roof of the furnace. This shaft is fitted with a stationary hollow casing formed of a material which contains a high percentage of Pt.

ELECTRICAL AND ELECTRONIC ENGINEERING

Electric Switching Device with Contacts

PHILIPS ELECTRONIC & ASSOCIATED INDUSTRIES LTD. *British Patent 1,451,124*
Reed contacts are coated with a 0.1 μm thick Au layer and provided with Ru particles by immersion in a suspension of Ru powder in freon, and the contacts are then hermetically closed in an envelope.

Electron-Emission Cathode

U.S. SECRETARY OF THE NAVY *U.S. Patent 3,971,110*
An electron-emitting cathode containing a matrix of Ir or another Pt group metal is produced by mixing the matrix metal with Ag powder, shaping the mixture and then sintering the electrode at a temperature where the Ag evaporates. The active material, such as Ba, is deposited in the pores of the matrix.

Electrical Connection to a Molten Glass Container

JOHNSON MATTHEY & CO. LTD. *French Appl. 2,286,114*
A combined method of electrical connection and thermal gradient control is described in which a lug made of a low resistance alloy of one of the Pt group metals, Al, Cu, Ag or Au is immersed

in a bath of liquid metal alloy such as Ga-In-Sn eutectic held in a Cu reservoir. The method is useful in applications where a rigid mechanical connection produces excessive strain. An example of use is in the manufacture of glass fibre.

Electrical Resistance Element

JOHNSON MATTHEY & CO. LTD. *Dutch Appl. 76.02012*

Temperature sensitive resistance elements for resistance thermometers having a robust construction and exhibiting stable temperature coefficients of resistance are formed on the outside and/or inside of a tubular or cylindrical element of electrically non-conducting material. The electrical track is deposited as a spiral, zig-zag, crenellated or other elongated path and is composed of a layer of fused vitreous material containing a particulate metallic conducting phase. The metallic particles are selected from Au, Ag, Pt, Pd, Rh, Ir, Ru, Fe, Co, Ni, Cu and alloys thereof. The device may be used in I.C.E. exhaust or fuel injection control.

TEMPERATURE MEASUREMENT

High Temperature Electrostatic Probe

BRITISH LEYLAND TRUCK AND BUS DIVISION LTD. AND LOUGHBOROUGH UNIVERSITY OF TECHNOLOGY *British Patent 1,447,046*

The probe includes an electrical conductor extending longitudinally inside a ceramic tube. A ceramic plug terminates one end of the conductor and a Ni-P alloy coating covers the external surface of the tube and the exposed external surfaces of the plug. The outer surface of the tube is activated with PdCl_2 .

Semiconductor Temperature Sensor

R.C.A. CORP. *British Patent 1,450,265*
The sensor consists of a body of semiconductive material having a region of uniform resistivity, and means for supporting the body and making electrical contact to the region consisting of cantilevered beam leads, formed of successive layers of Ti, Pt or Pd, and Au and a reinforcing layer also of Au, connected to spaced areas of the region.

MEDICAL USES

Dental Restoration Combining Dental Porcelain and Improved White Gold Alloy

PENNWALT CORP. *U.S. Patent 3,961,420*
A dental restoration consists of a cast white Au alloy metal base in the shape of a tooth. The alloy consists of 50-54% Au, 27-31% Pd, 11-16% Ag, about 0.05-0.25% of Ir or Ru and a total of 4.5-8% In and Sn. Dental porcelain covers the metal base and is baked on to it.