ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Metastable Phase Formation and Decomposition in a Rapidly Solidified Aluminium-Platinum Alloy
X-ray diffraction and electron microscopic studies of the metastable phase formation and decomposition of a rapidly solidified 28% Pt-Al alloy were performed. Two metastable phases were detected. The first one was of a cubic structure with a=5.67Å and was a metastable extension of the equilibrium Al,Pt phase. The second phase, of the composition Al,Pt, was orthorhombic with a=15.76 Å, b=12.10 Å and c=8.31 Å.

Silicide Formation with Bilayers of Pd-Pt, Pd-Ni, and Pt-Ni
X-ray diffraction studies of the silicide formation of evaporated two-layered thin films of Pd-Ni, Pt-Ni and Pt-Pd on single-crystal Si, vacuum annealed at 200-900°C, were carried out. The silicide layers were highly inhomogeneous for annealing below 600°C but became homogeneous at >700°C. The silicide-substrate interface showed varying sharpness depending upon substrate orientation and evaporation sequence. The existence of ternary monosilicides of the type Pt,X,PdSi, Pt,X,NiSi, and Pd,X,NiSi is reported. The Pt,X,PdSi ternary silicide was stable up to 900°C.

Magnetic Properties of CePt3, between 4.2 and 295 K
The magnetic susceptibility of CePt3 was measured between 4.2 and 295 K by the Faraday method. The deviation from Curie-Weiss behaviour below 80 K can be explained by hexagonal crystal field splitting in the J=5/2 ground term of Ce3+

Phase Transformations in High-Strength Alloy of Palladium with Copper and Gallium
The phase transformations in 79.8 Pd-11.7 Cu-8.5 wt. % Ga alloy were studied after deformation and annealing at 380°C. The increased strength of this alloy is due to the precipitation of (Pd, Cu)3Ga with a b.c.c. structure.

Investigation of Alloy Systems Pd3AlCu-PdAl
Metallographic and differential thermal studies of the Pd3AlCu-PdAl system were performed. No restriction in growth of Pd3AlCu and PdAl compounds by solutes occurred in liquid or solid compounds immediately after solidification. The character of interactions of high temperature modified compounds of Pd3AlCu and PdAl are described by a diagram of a eutectoid type with the eutectoid point at 20 mol % PdAl and 770°C. At 556-440°C alloys transform into the solid compounds, subsequently undergoing polymorphous transformation into PdAl compounds and at 290°C into Pd3AlCu compounds.

Indentation Recovery of Amorphous Materials
Samples of Pd0.75Si0.25Cu and amorphous alloy, polystyrene and pyrex glass were indented by a cone shaped diamond, measured, and then annealed at various temperatures to allow the indentations to disappear. It was found that for Pd0.75Si0.25Cu an indentation of 0.5 μm deep did not change in depth after 24 minutes at 389°C. Since the crystallisation temperature is 410°C, annealing could not be carried out at higher temperatures or longer times without risking the uncertainty of crystallisation. This recovery was much slower than polystyrene or pyrex.

Dynamics of Laser-Induced Formation of Palladium Silicide
The formation of Pd silicide by laser irradiation of a thin Pd film evaporated on single crystal Si was studied. Silicide formation takes place through interdiffusion of the molten elements, followed by thermal quenching. A diffusion constant of 4 x 10^{-11} cm²/s was estimated. The reacted layer consisted of a mixture of different metal-Si compounds, including PdSi, Pd₃Si, Pd₂Si and Pd₃Si. By appropriate choice of Pd film thickness and laser pulse parameters either complete mixing of Pd and Si or tailored concentration profiles can be achieved. Pd₃Si is a commonly used silicide for ohmic contacts to Si semiconductor devices.
**Behaviour of Rhodium and Iridium during Carbonylation of Copper-Nickel Sulphidised Alloys**


The behaviour of Rh and Ir was studied during synthesis of Ni carbonyl from Cu-Ni sulphide materials. Rh and Ir were present only in the metallic phase with Rh uniformly dispersed throughout while Ir was concentrated in localised sections, isomorphically replacing Cu. Rh reacted with Cu sulphide yielding Rhs, phases containing > 5 at.%. Ir did not go through any changes, passing over into the solid residue of the synthesis.

**Thermodynamic Investigations in the Thorium-Osmium and Thorium-Iridium Systems**

H. KLEYKAMP, J. Less-Common Metals, 1979, 63, (1), P25-P33

The Gibbs energies of formation of the three intermetallic phases, ThOs₃, Th₃Os₂ and Th₂Os₂ occurring in the Th-Os system, and the ThIr₂ and Th₃Ir₃ phases of the Th-Ir system, were determined by e.m.f. measurements using solid galvanic cells with a CaF₂ electrolyte. The enthalpies of formation were correlated with calculated values based on thermodynamic models. The regions of the phase diagrams rich in noble metals for both systems were supplemented by pyrometric melting point determinations: ThOs₂, 2480°C; Th₃Ir₂, 2260°C; and Th₃Ir₃, 2280°C.

**CHEMICAL COMPOUNDS**

The Interaction of Pt(II) cis- and trans-Diaciddiammine with Sulphur Containing Dipetide


The interactions of cis- and trans-[Pt(NH₃)₂Cl₂], and also cis-[Pt(NH₃)₂(H₂O)₂][NO₃]₂ with S containing dipetides (LH₃)-glycyl- and x-alanylthimethionine with molar ratio 1:2, were studied. The chemical properties of the obtained complexes and also their molecular electrical conductivity and absorption spectra were given.

A New Cationic Binuclear Trihydrido Complex Containing One Four- and One Five-Coordinate Platinum Atom


An unusual binuclear Pt trihydrido complex was synthesised. This complex contains both a dihydrido bridge and a terminal hydride ligand.

This is the first example of a class of binuclear Pt hydrides containing one four- and one five-coordinate metal centre.

**Palladium(II) and Platinum(II) Complexes with Nucleobases and Nucleosides. Crystal Structure of trans-Bis(adeninato)bis(tri-n-butylphosphine)palladium(II)**


The synthesis and degradation of novel dinuclear and tetracuclear complexes [L(n-Bu₃P)MC1]₂ and [Cl₂(n-Bu₃P)M(L)₂M[P-n-Bu₃]Cl]₂, [M = Pt(II), Pt(II)] with the anion of adenine (L) have been studied. These complexes have nucleobases and nucleosides.

**Planar Complexes of Asymmetrically Substituted Alkyl and Atyl-α, β-dionedioximes with the Ions Nickel(II), Palladium(II) and Platinum(II)**


New planar bis(α, β-dionedioximato)metal(II) complexes of the ions Pd(II), Pt(II) and Ni(II) with asymmetrically substituted glyoximes as ligands are reported. These are found to crystallise in columnar stacks. Compared with the known symmetrical derivatives the solubility of the isolated neutral compounds greatly increased in organic solvents.

**On the Synthesis and Characterization of Pd(CO)(PPh₃)₃**


Pd(CO)(PPh₃)₃ could be isolated from the reaction mixture arising from cyclohexene hydrocarboxylation by PdCl₂(PPh₃)₂ as the catalyst precursor and also through direct reaction of Pd(PPh₃)₄ with CO in benzene. ³¹P- and ¹³C-NMR studies of this complex suggest a rapid dissociation of PPh₃ at room temperature and tetrahedral structure at -70°C in solution.

**Kinetics of Olefin Arylation with bis-(Triphenylphosphino) Palladium(II) Diacetate and Its trans→cis-Isomerisation**


Studies of the kinetics of Pd(PPh₃)₂(OAc)₃ decomposition with formation of Pd⁺ and of the kinetics of arylation of substituted styrene in the presence of Pd(PPh₃)₂(OAc)₂ in freezing HOAc were carried out. A mechanism of arylation is proposed, including intermediate reduction of Pd(II) to Pd⁺ with formation of σ-phenyl-palladium particles and a fast phase of transmission of phenyl groups from these particles onto olefins. Kinetics and conditions of trans→cis-isomerisation of Pd(PPh₃)₂(OAc)₂ are discussed.
Synthetic Aspects of Rhodium(III) Chemistry. I. A High Yield Route to cis-Bis(1,2-diaminoethane)rhodium(III) Complexes

A crude, 1:1 mixture of trans- and cis-[RhCl(en)2]ClO4 (en = 1, 2-diaminoethane) was obtained in ~80% yield following the pH controlled reaction of RhCl₃·3H₂O with en (as en, 2HCl). The crude mixture was converted to [Rh(ox)en]⁺(A) (ox = oxalate) isolating oxalato complex as pure perchlorate on bromide salts in ~80% yield. The cis-dihalo complex was synthesised in an almost quantitative yield by the reaction of (A) in boiling 6M HCl. The entire reaction sequence permitted the synthesis of the cis-dihalo complexes in ~60% overall yield based on RhCl₃·3H₂O.

U.V. Photoelectron Spectral Studies on the Metal Carbonyl Cluster Compounds Os₄(CO)₁₂, Ru₄(CO)₁₃, and Os₈(CO)₁₈

The photoelectron spectra of Os₄(CO)₁₂ and Ru₄(CO)₁₃ have been recorded and are consistent with the molecular orbital scheme proposed for such molecules. The first ionisation energies of these compounds, and of Os₈(CO)₁₈, were compared with the work functions of the corresponding metals and found to be ~3eV higher.

Ternary Metal Borides [La, Ce, Pr, Nd, Sm] Os₃B₄ and [Y, La, Ce, Pr, Nd, Sm, Gd, Tb] Ir₄B₄ with NdCo₂B₂-Type Structure

New ternary metal borides with composition R.E.T₄B₄ (R.E. = rare earth metal, T = transition metal) were prepared within the systems [La, Ce, Pr, Nd, Sm]-Os-B and [Y, La, Ce, Pr, Nd, Sm, Gd, Tb]-Ir-B. All compounds crystallised in the NdCo₂B₂-type structure.

ELECTROCHEMISTRY

The Measurement of Strong Adsorption on Platinum Film Electrodes by Surface Conductance

The adsorption of thiourea (TU), urea and sulphide on Pt-film electrodes was measured at 25 ± 1°C with 0.5M H₂SO₄ as supported electrolyte. The small dependence of ΔG on the potential for a monolayer of chemisorbed O₂ (1.6-0.8V), S(0.05-1.0V) or I(0.05-0.4V) shows that for these chemisorption monolayers the partial charge transfer coefficient does not depend on electrode potential.

Two Forms of Chemisorbed Sulphur on Platinum and Related Studies

The effect of temperature on the potentiodynamic oxidation of adsorbed S layers on Pt, by H₂S or SO₂ was studied. The broad oxidation peak at 1.2-1.3V observed at room temperature changed at 80°C. Two distinct peaks were observed: oxidation peak I (at 0.97V) and oxidation peak II (at 1.10V) corresponding to the weakly and strongly bound S, respectively. An extension of the H region was observed at higher temperatures during cathodic charging in the presence of adsorbed S.

Purification of Acetic Acid
Res. Discl., 1979, (177), 8

To reduce the by-product propionic acid formed when H is present during the production of acetic acid from methanol, a membrane, selectively permeable to H, is employed. The membrane can be made of Pd or Pd-Ag foils, or organic materials, or may be a multicomponent membrane. This effectively reduces H content after recycling the gases.

ELECTRODEPOSITION AND SURFACE COATINGS

A New Method for Coating Metals with Hydrogen-Transparent Pd Layers
T. Schober and A. Karl, J. Less-Common Metals, 1979, 63, (1), P53-P56

A new technique for coating metals with H-transparent Pd layers consists of spot welding a thin 25 µm foil onto the metal which is to be charged with H or D. The advantages of this method include: not having to use UHV equipment or degassing units for applying the Pd layer.

HETEROGENEOUS CATALYSIS

Evaluation of Catalysts for Vapour Phase Oxidation of Odorous Organic Compounds

The oxidation of four organic odorants: n-butanol, n-butyraldehyde, n-butyric acid and toluene was carried out over four commercially available catalysts: 0.1% Pt/γ-Al₂O₃, 0.5% Pd/γ-Al₂O₃, 0.5% Pt/γ-Al₂O₃ and 10% CuO/γ-Al₂O₃ at 116-497°C. The results show that the Pt catalysts are more effective in terms of chemical conversion as well as odour removal efficiency than the Pd and Cu catalysts which required much higher temperatures than the Pt catalysts for comparable performance.
Effect of Carbon on the State of Platinum in Aluminium Oxide Supported Bimetallic Catalysts

The effect of C on the state of Pt in 2 wt.% Pt/γ-Al₂O₃ bimetallic catalysts promoted by 0.8 wt.% Ir, 0.8 wt.% Re and 0.3 wt.% Ga was studied, on samples prepared by saturation in solutions of H₂IrCl₆, NH₄ReO₄ or Ga(NO₃)₃, before and after coking. The promoter was found to react with the support, filling vacant positions in the spinel structure of Al₂O₃.

Fluorinated Alumina-Platinum Catalysts in Decane Isomerisation

Studies of the effect of the method of the introduction of F on the catalytic activity and physico-chemical properties of fluorinated Pt/γ-Al₂O₃ catalysts prepared by treatment of γ-Al₂O₃ with HF followed by saturation with Pt, and by treatment of Pt/γ-Al₂O₃ with HF or with a fluororganic compound were performed during decane isomerisation at 40 atm and 325-400°C. Dispersion of Pt increased in Pt/γ-Al₂O₃ catalysts treated with F but their acidity was not affected. The Pt/γ-Al₂O₃ catalysts treated with HF were most active.

Poison-Resistant Catalysts for the Simultaneous Control of Hydrocarbon, Carbon Monoxide, and Nitrogen Oxide Emissions

The operation of Pt, Rh and Pd catalysts in automobile exhausts near the stoichiometric air:fuel ratio (A/F) was investigated. The extent of intrapellet diffusion limitations as a function of feedstream stoichiometry, poisoning mechanisms, the effects of Pt, Rh and Pd impregnation profiles on activity and poison resistance, and the effects of A/F oscillations on catalyst performance were examined. A pellet configuration containing an external shell of Pt and internal rings of Rh and Pd had improved poison resistance and light off characteristics. The addition of Ce improved the initial performance of the catalysts.

Rhodium Oxide Formation on the Surface of Pt-Rh Gauzes Used in the Catalytic Oxidation of Ammonia
M. Pszonicka, J. Catalysis, 1979, 56 (3), 472-474

90% Pt-Rh gauzes were used for NH₃ oxidation and then examined. The spent catalyst wires were found to be sheathed with a Rh oxide film of 8-10 μm thickness, much thicker than previously observed, of three different layers. This oxide layer explains the decrease of catalyst activity.

Study of Irradiated Pd/γ-Al₂O₃ Using the ESR Method

Spectroscopic studies of the mechanism of activity of γ irradiated 0.5-10% Pd/Al₂O₃ catalysts were performed during reduction at 500°C. Sorption ability of the catalyst increased due to the formation of ionic centres of activity after irradiation. The formation of Pd⁺ ions in the catalysts was found to have a fundamental effect on their activity and selectivity.

Carbonylation of Olefins in the Presence of Supported Palladium Catalysts

Carbonylation of olefins on supported Pd/C, Pd/zeolites, Pd:0.8 CaNaY and Pd:SiO₂ catalysts was performed at various temperatures and pressures. Pd/C and Pd/zeolites catalysts containing 0.25-1%, Pd were active and selective during carbonylation of ethylene, propylene and hexene-1 yielding carboxylic acid.

Activity of RhNaX Catalyst Promoted by Some Transition Metal Oxides in the Carbonylation of Methanol by Carbon Monoxide at Atmospheric Pressure

Studies of the effect of addition of Cr, Mn, Fe, Co, Ni and Cu on the catalytic activity and selectivity of Rh/zeolite NaX catalysts were performed during carbonylation of methanol by CO at atmospheric pressure. The formation of methyl acetate was observed at 210-240°C over catalysts promoted by Fe, Cu and Mn oxides with the selectivity of 92-100% and methanol conversion of >90%. The reaction was zero order for CO and CH₃OH and first order for CH₂O.

Versatile Polymer-Bound Hydrogenation Catalysts. Rhodium(I)-Catalyzed Hydrogenation

The bidentate ligand anthranilic acid was anchored to polystyrene beads and its Rh(I) complex prepared. This polymer catalyst has exceptional hydrogenation activity, long-term stability, and insensitivity to poisoning. Hundreds of catalytic cycles per metal atom are demonstrated without substantial loss of activity. The Rh catalyst reduces various olefinic and aromatic hydrocarbons and carbonyl, nitrile and nitro functional groups. Catalytic activity depends on retention of beads, if fragmentation occurs the activity is diminished.
Adsorption Properties of Osmium Catalysts


Microcalorimetric, thermal desorption and electron microscopy studies of the H₂ adsorption on Os catalysts were performed. The adsorption temperature of H₂ increases over Os/Al₂O₃ catalysts compared to that over Os/black catalysts. The adsorption temperature of H₂ on Os catalysts was higher in the gaseous phase than in the liquid phase due to the chemisorption effect of H₂O.

Kinetics of the Methanation Reaction over Ru, Ru-Ni, Ru-Cu, and Ni Clusters in Zeolite Y

D. J. ELLIOTT and J. H. LUNSFORD, *J. Catalysis*, 1979, 57, (i), 11-26

Clusters of Ru, Ni and Ru-Ni, and Ru-Cu bimetallics in a Y-type zeolite were investigated as catalysts for the reaction of CO with H₂ to form CH₄. Ni clusters had smaller turnover numbers than the Ru clusters. Adding Ru to the bimetallic clusters caused average particle size to decrease, and Ru-Ni zeolite turnover numbers decreased linearly as Ni was added.

Catalysis by a Ruthenium Complex Heterogenized in Faujasite-Type Zeolites: the Water Gas-Shift Reaction


The Ru(NH₃)₂⁺ complex, exchanged as such in faujasite-type zeolites, can be converted into another kind of complex of the form \([\text{Ru(NH}_3\text{)}_2\text{(OH)}_x\text{(CO)}_y]^{3+}\) with \(x < 3\); this complex, which is stable up to 280°C, has no homogeneous equivalent. It is very active for the water gas shift reaction and it has greater activity than a Cu based low-temperature shift catalyst.

Homogeneous Catalysis

Selective Codimerization of Acetylenes and Allyl Halides Catalyzed by Palladium Complexes


The reaction of various acetylenes and allyl halides with Pd complexes selectively gives substituted 1,4-diene codimers. The PdX₂(PPh₃)₃ complex is the most active catalyst. In contrast to substituted acetylenes, the reaction of acetylene and allyl halides gives a cotrimer besides codimers. The catalysis proceeds initially by acetylene inserting into a Pd-halogen bond and subsequently allyl halide inserts into a Pd-alkyl bond, followed by β-halogen elimination to give a codimer.

Hydrogenation Catalysts—Their Effect on Selectivity


A review of the effects of heterogeneous (including the platinum group metals) and homogeneous catalysts including a mixture of chloroplatinic acid and tin (II) chloride, \([\text{Pt(PPh}_3\text{)}_2\text{(SnCl}_3\text{)}\text{H}]\), RuCl₃(PPh₃)₂ in isopropyl alcohol and other Pt and Pd catalysts, etc. on the hydrogenation of edible oils is discussed. (107 Refs.)

Effect of Partial Pressures of Hydrogen and Carbon Monoxide on Hydroformylation of Cyclododecene in the Presence of Hydrocarbonyl-tris(Triphenylphosphine) Rhodium (I)


Studies of the effect of partial pressures of H₂ and CO on hydroformylation of cyclododecene in the presence of RhH(CO)(PPh₃)₂ with and without surplus PPh₃ at 11.5-120 atm and 100°C were performed. An increase in the reaction rate with an increase in H₂ and CO partial pressures when the Rh catalyst contained no surplus PPh₃ was observed. The rate of the hydroformylation reaction in the presence of the Rh catalyst containing excess PPh₃ depends only on the partial pressure of H₂ but not on the partial pressure of CO.

Infrared and Kinetic Study of Polymer-Bound Rhodium Cluster Catalysts for Hydrogenation


Polymers prepared by ligand exchange of poly(styrene-diyvinylbenzene) membranes containing bond PPh₃ groups and Rh₃(CO)₁₄ were found to be active cluster catalysts for the hydrogenation of ethylene and cyclohexene at 75°C and 1 atm. The kinetics of the cyclohexene hydrogenation were second order in cyclohexene partial pressure and one-half order in H₂ partial pressure.

Glass Technology

Phase Separation and Crystallization in Amorphous Pd-Si-Sb


Replacing some of the Si in a Pd-Si-Sb glass with Sb makes it more resistant to crystallisation than binary Pd-Si. This is shown by an increase in crystallisation temperature and a decrease in glass temperature as Sb content is increased. Alloys such as Pdₓ₋₁Sᵣ₋₁₋₁₋₁₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋˓—
Wires of Pd$_{77.5}$Cu$_8$Si$_{18.5}$ metallic glass were cold drawn using diamond dies. A total area reduction of up to about 93% was obtained after multiple passes through appropriate dies. Tensile tests conducted on both drawn and undrawn wires show fracture in planes that always deviate from the 45° maximum shear phase. The fracture stresses of drawn wires are found to be slightly increased; the macroscopic elongation to break increases considerably after cold drawing.

**ELECTRICAL AND ELECTRONIC ENGINEERING**

Contact Reactions in Pd/GaAs Junction


X-ray diffraction studies of the solid-state reaction of thin Pd films with GaAs substrates were performed. Fast diffusion and dissolution were observed for both As and Ga into Pd, which slowed down after the formation of distinct compound layers. These were identified as PdAs$_2$, PdGa at 250°C, PdAs$_3$, PdGa and Pd$_3$Ga at 350°C and PdGa at 500°C.

**NEW PATENTS**

**METALS AND ALLOYS**

-Palladium-Containing Brazing Alloy

INTERNATIONAL BUSINESS MACHINES CORP.

_British Patent_ 1,539,686

Improved ferromagnetic alloys for use such as in bubble domain devices have the general formula Ni$_{100-x}$Fe$_x$Pd$_y$, where x is 25-80 at. % and y is 25-65 at. %.

-Nickel Glow Plug Alloys

NGK SPARK PLUG COMPANY LTD.

_British Appl._ 2,003,501

An alloy for use in a glow plug heater used in I.C.E., particularly diesel engines, contains Ni and between 0.05 and 2.0% of Y, Zr and/or Ru. The additions prevent grain coarsening and high temperature degradation without affecting the electrical resistance of the material.

-Amorphous Alloys

SONY CORP.

_British Appl._ 2,003,772

A continuous-casting process for the manufacture of amorphous alloys is applicable to Fe-P-C alloys containing minor amounts of Ru, for instance Fe$_7$,Ru$_{0.8}$.P$_{17}.C$_7.

**CHEMICAL COMPOUNDS**

-Ruthenium and/or Iridium-Containing Pyrochlore Compound

EXxon RESEARCH & ENGINEERING CO.

_U.S. Patent_ 4,129,525

Electrically conductive pyrochlore compounds have the formula A$_x$(B$_{1-x}$A)$_{1-y}$O$_7$ where A is Pb and/or Bi, B is Ru and/or Ir, x is 0-1.0 and y is 0-1.0.

-Adhesive Organopolysiloxanes

WACKER-CHEMIE G.m.b.H. _U.S. Patent_ 4,130,707

The adhesive compounds contain vinyl-containing organopolysiloxanes, organopolysiloxanes containing Si-H atoms and Group VIII metal