

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

The Kinetics of Platinum Dissolving in Molten Copper. (The Rotary Disc Method)

T. E. MARDER, E. L. LUBININ, A. I. TIMOFEEV and A. L. SHUNIN, *Izv. Vysshikh Ucheb. Zaved., Tsvetnaya Metallurgiya*, 1977, (1), 151-153

The dissolution of Pt in molten Cu was studied using the rotary disc method at 1150-1300°C. The results show that the rate of Pt dissolution is 0.005-0.13 g/cm²s. The dissolution of Pt in Cu was found to take place by diffusion. The diffusion coefficients are derived.

The Influence of Static Stresses on Ordering of the CuPt Type Alloys

A. K. KANYUKA, *Fiz. Metal. Metalloved.*, 1977, 43, (3), 493-497

The influence of uniform static stresses, caused by external loading, on the temperature of the order-disorder phase transition in an alloy of the CuPt type is discussed.

Ageing Characteristics of Aluminium Wire Bonds on Thick Film Platinum-Silver Metallisation

S. KHADPE, *Insulation/Circuits*, 1977, 23, (2), 23-24

The ageing characteristics of Al wire bonds on Pt-Ag metallisation was determined using a bond strength vs. ageing time at 150°C plot. The results show that the bond strength does not decrease significantly with ageing at 150°C. After 1000h of ageing more than 80% of the initial bond strength was retained. The Pt-Ag conductor materials can be used as substitutes for Au and Pd-Ag materials.

An Investigation of High Temperature Thermodynamic Properties in the Pt-Zr and Pt-Hf Systems

P. J. MESCHTER and W. L. WORRELL, *Met. Trans.*, 1977, 8A, (3), 503-509

The thermodynamic properties of 2-25 at.% Zr-Pt and 20-25 at.% Hf-Pt alloys were studied at 1100-1400K using a galvanic cell technique with a ThO₂-based electrolyte. The results show that the activities of Zr and Hf exhibit large negative deviations from Raoult's Law. The standard free energies of formation, G_f⁰, for the intermetallic compounds ZrPt₃, ZrPt₂ and HfPt₃ at 1300K were found -92.680, -91.740 and -97.350 cal/mole, respectively. Possible applications in fuel cells and thermocouple systems are discussed.

The Superconducting Properties of PdH_x_{x<1}

D. S. McLACHLAN and T. B. DOYLE, *J. Low Temp. Phys.*, 1977, 26, (3/4), 589-601

The superconducting parameters of PdH_x (x=H/Pd=0.9801-0.9957) foils were determined using measurements of the magnetisation curves and resistive transitions in magnetic fields at 2-10.4K. The results show that PdH is a type I superconductor with a T_c of 10.2-10.4K, H_c(0) < 900G and x~0.6 at absolute zero. PdH_x becomes a type II superconductor for x < 0.995, due to the increasing resistivity of the material.

The 50K Transition in Palladium Hydrogen Alloys: II. Specific Heat and Thermal Relaxation

J. K. JACOBS and F. D. MANCHESTER, *J. Phys. F: Metal Phys.*, 1977, 7, (1), 23-33

Studies of the specific heat anomaly at 50K in Pd-H β-phase samples show that the magnitude of the anomaly depends on the rate of temperature change used in the specific heat measurements—the slower the rate, the larger the anomaly. The data of the spontaneous heat released by the Pd-H sample after sudden cooling to temperatures in the 50K region showed a thermal relaxation in Pd-H with fast and slow relaxation times and a common activation energy of (1.98 ± 0.03) × 10³Jg/atom of H.

Influence of Deformation on the Low-temperature Specific Heat of a Dilute α-Phase Pd-H Alloy

U. MIZUTANI, T. B. MASSALSKI, J. BEVK and R. R. VANDERVOORT, *J. Phys. F: Metal Phys.*, 1977, 7, (3), L63-L68

Low temperature specific heats were measured at 1.5-4.2K in α-phase Pd-H sample of H/Pd ratio 0.005 in two different conditions: after deformation at room temperature, and after deformation at liquid N temperature and a short ageing at room temperature. The value of the electronic specific heat coefficient in the latter case was found to be close to that of pure Pd, suggesting the formation of β hydride.

Solution of Hydrogen in Palladium/Copper Alloys

D. FISHER, D. M. CHISDES and T. B. FLANAGAN, *J. Solid State Chem.*, 1977, 20, (2), 149-158

Studies of the solution of H₂ in Pd-Cu f.c.c. substitutional alloys at low H₂ content show that the relative partial molar enthalpies of absorption at infinite dilution are less exothermic for the alloys than for Pd. It was found that interstitial

H₂ increases the relative electrical resistance to a lesser extent with increase of X_{Cu}, but the absolute increase of resistance is nearly invariant with X_{Cu}.

Direct Observation of Pd/MgO and Pd/SiO₂ Reactions in the Transmission Electron Microscope

A. F. MOODIE and C. E. WARBLE, *Phil. Mag.*, 1977, **35**, (1), 201-211

Studies of the surface reaction between Pd and MgO and Pd and quartz at temperatures below the melting point of the metal were carried out using a transmission electron microscope. It is shown that for Pd/MgO the reacting phase has liquid-like characteristics, while the ceramic remains strain-free both during and after the reaction. In the case of Pd/SiO₂, the reaction is similar with the exception that small amorphous regions develop randomly over the surface which later move, disperse and sometimes coalesce into droplets. A bond between the metal and the ceramic was found to exist.

Nickel-Palladium-Germanium Alloys

W. WOPERSNOW and K. SCHUBERT, *J. Less-Common Metals*, 1977, **52**, (1), 1-12

Crystal structure studies of the Ni-Pd-Ge alloys show that Ni may be substituted for Pd up to the composition Ni₂₇Pd₄₀Ge₃₃ in the Pd₂Ge phase. A phase with the composition NiPdGe having the PbFCl type of structure is formed below 600°C. A phase of composition Ni₂Pd₄Ge₃ having an Fe₂P type of structure forms below 500°C.

The Niobium-Gallium-Iridium System. I. Phase Equilibria at 1000°C and Superconductivity in the Niobium-rich Part of the System

M. DRYES, *J. Less-Common Metals*, 1977, **52**, (1), 81-85

X-ray diffraction and electron microprobe techniques were used to study the phase equilibria at 1000°C in the Nb-rich section of the Nb-Ga-Ir system. The results show that complete solid solubility exists between Nb₃Ir and Nb₃Ga while the σ-phase and Nb₃Ga₃ form limited solid solutions. The superconducting transition temperatures were also determined.

Some Properties of Alloys of the Ti-Ru System

N. G. BORISKINA and I. I. KORNILOV, *Izv. Akad. Nauk S.S.S.R., Metall.*, 1977, (1), 193-197

Studies of the changes of hardness, specific resistance and thermoelectromotive force of Ru-Ti alloys in the as cast state and also after quenching from 1100 and 860°C and annealing at 600 and 400°C were carried out. The results show that the changes take place as a result of phase composition changes of the alloys. The alloys with the δ-phase structure, having high e.m.f. values can be practically used for instrument making.

X-ray and Microspectroscopic Studies of the RuO₂-TiO₂-Cl System

YU. E. ROGINSKAYA, V. I. BYSTROV and D. M. SHUB, *Zh. Neorg. Khim.*, 1977, **22**, (1), 201-205

X-ray and microspectroscopic studies of the quasi-binary RuO₂-TiO₂-Cl system were made using Ru-Ti oxide layers containing 25, 50 and 75 wt.% RuO₂ deposited from Ru and Ti chloride solutions on quartz or Ti substrates. The results showed the formation of solid solution with the rutile type structure. When the Cl concentration was ~0.1 at.%, the solid solution decomposed into two rutile phases at >800°C: RuO₂ and TiO₂ phases accompanied by the increase in the crystallisation of these phases.

CHEMICAL COMPOUNDS

The Enneacarbonyls of Ruthenium and Osmium

J. R. MOSS and W. A. G. GRAHAM, *J. Chem. Soc., Dalton Trans.*, 1977, (1), 95-99

Studies of the u.v. irradiation of *n*-heptane solutions of the pentacarbonyls of Ru and Os at -40°C were carried out. It is shown that in the case of [Os(CO)₅] the newly isolated carbonyl compound [Os₂(CO)₉], decomposes slowly in solution. The new compound [Ru₂(CO)₈] which is a product of the low temperature irradiation of [Ru(CO)₅] is extremely unstable in both the solid state and in solution at room temperature.

Preparation and Characterisation of Members of a Homologous Series of Dihydrido-carbonyl Compounds of Osmium

J. R. MOSS and W. A. G. GRAHAM, *Inorg. Chem.*, 1977, **16**, (1), 75-79

The preparation of carbonyl hydrides H₂[Os(CO)₄]_n (n=1, 2 or 3) by the high pressure carbonylation of Os tetroxide in the presence of H₂ is described. A compound H₂Os₄(CO)₁₆ is also formed in this reaction. The preparation of dihydrides, H₂Os₂(CO)₈ and H₂Os₃(CO)₁₂, is also described and their structures are discussed.

ELECTROCHEMISTRY

The Oxidation of Carbon Monoxide at Platinum and Gold Metallised Membrane Electrodes

T. K. GIBBS, C. MCCALLUM and D. PLETCHER, *Electrochim. Acta*, 1977, **22**, (5), 525-530

Studies of the oxidation of CO at Pt and Au membrane electrodes show similar electrochemical characteristics to those of massive electrodes. The short time response at Pt is determined by the oxidation of a surface monolayer of CO by a reactant pair mechanism occurring at the edges of growing islands of an oxidised Pt species. The construction of an analytical device is discussed.

Activated Metal Anodes in Electrochemical Processes

J.-W. KUHN VON BURGSDORFF, *Chem. Ing. Tech.*, 1977, 49, (4), 294-298

Various activated metal anodes used in electrochemical processes are reviewed. The three stages of this development include the Ta-Pt anode for persulphate production, the platinised Ti anode and the "dimensionally stable anode" (DSA) consisting of a valve metal and a semi-conduction mixed oxide coating. The advantages of the DSA are shown in their application to the caustic chlorine electrolysis.

Preparation of Ruthenium Dioxide Electrodes and Their Anodic Polarisation Characteristics in Acidic Solutions

C. IWAKURA, K. HIRAO and H. TAMURA, *Electrochim. Acta*, 1977, 22, (4), 335-340

Studies of the anodic polarisation behaviour of anhydrous RuO₂ electrodes prepared by heating hydrous RuO₂ at different temperatures in acidic solutions showed that excellent anode material was obtained by heating hydrous RuO₂ in air at ~450°C. This electrode was quite stable and had strong resistance against the anodic dissolution together with very low overvoltage for the O₂ evolution. Generally, the electrode composed of poorly crystalline RuO₂ showed the good anodic polarisation characteristics.

The Reason for the Loss of Activity of Titanium Anodes Coated with a Layer of RuO₂ and TiO₂

T. LOUCKA, *J. Appl. Electrochem.*, 1977, 7, (3), 211-214

The loss of activity of two types of activated Ti anodes with a layer of RuO₂ only and with a layer of RuO₂ and TiO₂ prepared by applying ethanol solution of RuCl₃ or RuCl₃+TiCl₃ respectively was studied in 0.5N H₂SO₄ using the galvanostatic method. On the basis of the experimental data it is suggested that the ATA activity results from the formation of a non-conductive oxide film at the Ti-active layer interface.

LABORATORY APPARATUS AND TECHNIQUE

The Coulometric Determination of the Amount of Adsorbed Hydrogen as a Method of Measuring the Surface Area of Platinum Powders

T. C. FRANKLIN and Y. MIYAKOSHI, *Surface Technol.*, 1977, 5, (2), 119-134

The catalytic activity of Pt was measured using the coulometrically determined amount of H₂ that adsorbs on Pt black. This technique was used to measure the surface area of Pt black powders as catalysts for formaldehyde oxidation

and acetone hydrogenation. It is shown that the oxidation of formaldehyde takes place on sites associated with the strongly bonded hydrogen, while the hydrogenation of acetone occurs mainly on sites associated with the weakly bonded hydrogen.

HETEROGENEOUS CATALYSIS

The Relation of Actual Specific Activity of Platinum on Alumina Catalysts with Their Stability in Cyclohexane Dehydrogenation

N. M. ZAIDMAN, YU. A. SAVOSTIN and N. G. KOZHEVNIKOVA, *Khim. Tekhnol. Topliv Masel*, 1977, (2), 30-34

Studies of cyclohexane dehydrogenation over Pt/Al₂O₃ catalysts show that the deposition of C on these catalysts depends on the actual specific activity of these catalysts. The rate of coke deposition increases sharply with a decrease of the actual specific activity.

Activity and Selectivity of Bimetallic Catalysts in *n*-Hexane Aromatisation

YU. N. USOV, L. G. ZUBANOVA and N. I. KUVSHINOVA, *Neftekhimiya*, 1977, 17, (1), 69-75

The influence of Ga, Cd, Ge, Sb, Sn and Pb additions on the activity and selectivity of Pt/Al₂O₃ catalysts was studied in *n*-hexane aromatisation. The results show that the catalyst containing 0.25-0.5wt.% Pt and having Pt:Pb=1-2:1 gives the highest activity and selectivity for this reaction.

Hydrogenation of Styrene on a Pt/BaSO₄ Catalyst under Hydrogen Pressure

D. V. SOKOL'SKII and A. UALIKHANOVA, *Zh. Fiz. Khim.*, 1977, 51, (2), 492-494

The hydrogenation of styrene was carried out on a 5 at.% Pt/BaSO₄ catalyst in H₂O and in 96% ethanol at 10-50°C and at H₂ pressure 20-100 atm. It is shown that the reaction rate in ethanol increases with increasing H₂ pressure. The apparent activation energies remain practically constant at 8.3-7.9 kcal/mole. The reaction was found to be of zero order in the substrate at 20 and 80 atm. The reaction product, ethyl benzene, has no poisonous effect on the catalyst.

The Role of Ultraviolet Radiation in Promoting the Palladium-Catalysed Oxidation of Carbon Monoxide

B.-H. CHEN, J. S. CLOSE and J. M. WHITE, *J. Catalysis*, 1977, 46, (3), 253-258

Studies of the photoenhancement of the oxidation of CO over Pd were carried out at low and high pressures, and 300-443K. A marked photoenhancement of the rate occurred at a total pressure of 20 Torr while at below 10⁻⁴ Torr no increase was observed. The temperature dependence of the photoeffect is discussed.

Hydrogenation of Acetylene in Excess Ethylene on an Alumina Supported Palladium Catalyst in a Static System

W. T. MCGOWN, C. KEMBALL, D. A. WHAN and M. S. SCURRELL, *J. Chem. Soc., Faraday Trans. 1*, 1977, **73**, (4), 632-647

Studies of the kinetics of the hydrogenation of 2% acetylene in ethylene mixture on a Pd/Al₂O₃ catalyst in a static system showed that the produced ethane comes predominantly from the ethylene. It is suggested that two types of site exist on the surface: type X which hydrogenates both acetylene and ethylene and on which acetylene is adsorbed ~2200 times stronger than ethylene at 293K and type Y which is easily poisoned by CO and can hydrogenate ethylene even in the presence of acetylene.

A Mössbauer Study of Automotive Emission Control Catalysts

C. A. CLAUSEN and M. L. GOOD, *J. Catalysis*, 1977, **46**, (1), 58-64

The state of Ru in a series of barium oxide stabilised Ru automotive emission control catalysts was studied. The results show that the chemical form of the Ru in these catalysts is a mixture of RuO₂ and BaRuO₃. It was found that a loss in Ru stabilisation occurs during repeated oxidation-reduction cycling. It is suggested that this is due to the separation of Ru metal from the stabilising barium oxide phase.

Kinetics of Ternary Nitric Oxide Reduction on Ruthenium

R. SCHLEPPY and Y. T. SHAH, *Ind. Engng. Chem., Product Res. Dev.*, 1977, **16**, (1), 47-51

Studies of the reduction of NO and N₂O over a fibre glass supported Ru catalyst in a ternary mixture, NO-CO-H₂, were carried out. Feed concentration of the NO and N₂O were from 0.2 to 1.7 mole%, while those of the CO and H₂ were from 1.0-5.0 mole%. N₂O was found to be a significant intermediate of NO reduction at low conversions.

HOMOGENEOUS CATALYSIS

Transfer Hydrogenation and Transfer Hydrogenolysis. 13. Hydrogen Transfer from Cyclic Amines to Aromatic Nitro Compounds Catalysed by Noble Metal Salts

H. IMAI, T. NISHIGUCHI and K. FUKUZUMI, *J. Org. Chem.*, 1977, **42**, (3), 431-434

Studies of the homogeneous transfer hydrogenation of nitrobenzenes to anilines, using indoline as a H donor, showed that RuCl₃·H₂O and RhCl₃·3H₂O had high and PdBr₂ and PdCl₂ moderate catalytic activity. A mechanism is proposed in which the initial formation of Rh(I) species, the coordination of nitrobenzene to Rh(I) species and the hydrogen transfer from indoline to nitrobenzene are involved.

Reductive Coupling of Benzhydrols by Homogeneous Ruthenium Catalysts

I. PRI-BAR, O. BUCHMAN and J. BLUM, *Tetrahedron Letters*, 1977, (17), 1443-1446

A new RuCl₂(PPh₃)₃ catalysed H transfer reaction in which secondary carbinols undergo reductive coupling is reported. A number of Pt metal compounds were studied for the various transformation of benzhydrol at 200°C but only RuCl₂(PPh₃)₃ was found to be an effective catalyst for the reductive coupling. PdCl₂(PPh₃)₂ and PtCl₂(PPh₃)₂ promote only ether formation while RhCl(PPh₃)₃ gives a molar ratio of 1:2 of dibenzhydryl ether and 1,1,2,2-tetraphenylethane.

Complexes of the Platinum Metals. 7. Homogeneous Ruthenium and Osmium Catalysts for the Dehydrogenation of Primary and Secondary Alcohols

A. DOBSON and S. D. ROBINSON, *Inorg. Chem.*, 1977, **16**, (1), 137-142

Studies of the dehydrogenation of primary and secondary alcohols to aldehydes and ketones show that Ru and Os complexes [M(OCOR_F)₂(CO)(PPh₃)₂] (R_F=CF₃, C₂F₅ or C₆F₅) are useful catalysts for this process. Catalyst efficiency was found to decrease in the following order Ru > Os and CF₃ ~ C₂F₅ > C₆F₅ for a given alcohol under standard conditions.

FUEL CELLS

State and Action of the Tin Atoms in Platinum-Tin Catalysts for Methanol Fuel Cells

M. M. P. JANSSEN and J. MOOLHUYSEN, *J. Catalysis*, 1977, **46**, (3), 289-296

Studies of the behaviour and the kinetics of Pt-Sn electrodes in pure acid and during methanol oxidation were carried out using cyclic voltammetry. It is shown that the zero-valent Sn atoms influence the adsorption properties of the Pt atoms. The increase in methanol oxidation rate on Pt-Sn electrodes is explained in terms of a "ligand" effect.

CATHODIC PROTECTION

Platinum Consumption in Cathodic Protection Anodes

R. BABOIAN, *Mater. Performance*, 1977, **16**, (3), 20-22

Studies of the effects of current density and electrolyte composition on the corrosion of Pt-clad Nb base anodes were carried out in fresh and in salt water. It is shown that corrosion rates are roughly proportional to current density and are greater in fresh than in salt water. This is due to different anodic species in the two environments. The corrosion occurs as a result of oxide film formation on the Pt surface.

Increase of Passivity and Corrosion Resistance of Titanium by Alloying Its Surface with Palladium

N. D. TOMASHOV, G. P. CHERNOVA and T. A. FEDOSEEVA, *Zashchita Metal.*, 1977, **13**, (2), 164-169

Studies of the electrochemical behaviour and corrosion resistance of Ti modified by Pd electrodeposits (1, 5 and 10 μm thick) show its high passivity and corrosion resistance in 20-50% H_2SO_4 and 5-20% HCl at 100°C. The unmodified Ti in these conditions becomes fully corroded. It is shown that a Ti surface with electrodeposited Pd has a higher corrosion resistance in both acids than Ti+0.2%Pd alloy.

GLASS TECHNOLOGY

Effect of Some Manufacturing Conditions on the Optical Loss of Compound Glass Fibers

S. SHIBATA and S. TAKAHASHI, *J. Non-Cryst. Solids*, 1977, **23**, (1), 111-122

The production of low-loss optical glass fibres in Pt crucibles was studied and the effects of the Pt contamination and gas flow on the optical loss of compound silicate glass fibres were investigated. It is shown that when the concentration of Pt dissolved into the glass from the Pt crucible is >50 ppm, the optical loss is ~ 5000 dB/km.

NEW PATENTS

METALS AND ALLOYS

Electroconductive, Corrosion Resistant Silicon Alloys

P.P.G. INDUSTRIES INC. *British Patent 1,466,455*
A Si alloy has an electroconductivity greater than $100/\Omega\text{cm}$ and consists of 0.2-2% of a dopant selected from N, P, B and Al, 1-50% of a transition metal such as Ru, Rh, Os, Ir, Pt, Pd, Ag or Au, balance Si. The alloy has a structure in the form of a predominant, discontinuous, Si rich phase, continuous rivulets of a transition metal silicide rich phase surrounding the Si rich phase, and discrete nodules of a phase rich in the dopant material.

Re-orientation of Grain Stabilised Platinum

JOHNSON MATTHEY & CO. LTD.

U.S. Patent 4,002,503
The mechanical properties of a previously hardened Pt-Rh alloy which includes dispersed phase Zr oxide as a strengthening element are improved by cold working the composition at a temperature below that at which recrystallisation occurs and

ELECTRICAL AND ELECTRONIC ENGINEERING

Study of Al/Pd₂Si Contacts on Si

H. GRINOLDS and G. Y. ROBINSON, *J. Vacuum Sci. Technol.*, 1977, **14**, (1), 75-78

Studies of the interaction of an Al interconnect layer with Pd₂Si contacts on an *n*-type Si substrate show that the contact barrier energy Φ_{BN} decreased initially from ~ 0.71 to 0.65 eV. This decrease was shown to be due to the decomposition of the Pd₂Si layer. It is suggested that Al may enter the *n*-type Si as a compensating impurity during prolonged heat treatments.

MEDICAL USES

The Crystal and Molecular Structure of *cis*-Dichlorobis(cyclohexylamine)platinum (II)

J. IBALL and S. N. SCRIMGEOUR, *Acta Cryst. B*, 1977, **33**, (4), 1194-1196

Crystallographic studies of the anti-tumour agent, *cis*-dichlorobis(cyclohexylamine)Pt(II) show it to be orthorhombic with $a=26.12$, $b=6.660$, $c=8.981\text{\AA}$, $Z=4$, space group *Pbcn*. The Pt atom is surrounded by two N and two Cl atoms in a *cis* square-planar arrangement. The shortest Pt-Pt distance is 4.49Å.

then annealing. The recrystallisation which occurs during annealing results in an elongated grain structure highly oriented in the direction of working.

High Temperature-stable Metal Powder

JOHNSON MATTHEY & CO. LTD.

German Offen. 2,630,062

A metal powder which does not agglomerate or sinter at or around the melting point of the metal consists of a refractory substrate such as Al_2O_3 , SiO_2 or Si carbide coated with a Pt group metal, Au or Ag.

CHEMICAL COMPOUNDS

Osmium Tetroxide Complexes

JOHNSON MATTHEY & CO. LTD.

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Complexes may be formed from OsO_4 and compounds with a heterocyclic ring having one or two N atoms, such as phthalazine, and used for the fixing and/or dyeing of cells. The treated cells may then be examined by electron microscopy.