

# ABSTRACTS

## of current literature on the platinum metals and their alloys

### PROPERTIES

#### Low-energy Electron-diffraction Study of the Clean (100), (111), and (110) Faces of Platinum

H. B. LYON and G. A. SOMORJAI, *J. Chem. Phys.*, 1967, **46**, (7), 2539-2550

The (100), (111) and (110) faces of a "clean" Pt single crystal were studied as a function of temperature by LEED techniques in ultra-high vacuum. At low temperatures (111) and (100) show several ordered structures stable within a well-defined temperature range; the (110) face shows faceting above 600°C. Above 750°C a new stable phase is formed irreversibly on all three faces and is characterised by a ring diffraction pattern which increases in intensity as the m.p. of Pt is approached and is due to domains of (111) surface structure.

#### Surface Self-diffusion of Nickel and Platinum

A. J. MELMED, *J. Appl. Phys.*, 1967, **38**, (4), 1885-1892

Field-electron emission spectroscopy of Pt at 550-850°K indicated an Arrhenius-type relationship between temperature and time, so that activation energies of surface rearrangement could be derived:  $Q_f = 26.3 \pm 2.6$  kcal/mole in the range  $(27-39) \times 10^6$  V/cm for electric field build-up; zero field activation energy is calculated as  $29.7 \pm 3.0$  kcal/mole;  $Q_0 = 29.5 \pm 3.0$  kcal/mole for surface tension (annealing). Either type of measurement is satisfactory to  $\pm 10\%$ .

#### Platinum Oxidation Kinetics with Convective Diffusion and Surface Reaction

R. W. BARTLETT, *J. Electrochem. Soc.*, 1967, **114**, (6), 547-550

An analysis of the oxidation kinetics of Pt considered how the oxidation rate is affected by the reversible surface reaction  $O_2 + Pt \rightleftharpoons PtO_2(g)$  and by transport of the oxide vapour through a gaseous boundary layer, and derived mass transfer coefficients for oxide vapour diffusion, the forward and reverse specific rate constants for steady-state surface oxidation, and oxidation rate curves at various pressures and temperatures.

#### Ideal Resistivity of Platinum below 20°K

R. J. BERRY, *Can. J. Phys.*, 1967, **45**, (5), 1693-1708

The electrical resistivity of ideally pure Pt may be represented by a  $T^2$  (electron-electron) scattering term plus a second term proportional to  $T^{4.7 \pm 0.2}$  in the range 7-17°K and to  $\sim T^{4.7 \pm 0.5}$  in the range 3-7°K, where the general relation is

$W_{IT} = p_i T^2 + q_i T^5$  and  $W_{IT}$  is the resistance ratio  $R_{IT}/R_{i273.15}$  at T°K. Accurate measurements were made on Pt used for resistance thermometry. The two-band model was used to correct small but significant impurity scattering. The temperature dependence of the "ideal" resistivity function was compared with theory and previous work and some discrepancies were noticed.

#### Thermal Conductivity of Selected Materials

*U.S. Nat. Bur. Stds NSRDS-8*, 1966, (Nov.), 9-10, 45-50

Among the materials reviewed are Pt and 40% Rh-Pt. Curves for the variation of thermal conductivity with temperature are derived from work reported in the literature. Further work is needed to define the curves more accurately.

#### Heat-resistance of Platinum, Palladium and their Alloys

E. I. RYTVIN, V. M. KUZ'MIN and A. E. PETROVA, *Metalloved. term. Obrabot. Metal.*, 1967, (2), 31-32  
25%Pd-Pt had the greatest heat-resistance of Pt, Pd, Rh-Pt and Pd-Pt samples tested at 1200-1400°C with 0.5-1.0 kg/mm<sup>2</sup> axial stresses. Time-to-failure was recorded as a measure of heat-resistance and curves for Pd-Pt showed sharp maxima, particularly at lower temperatures.

#### Deformation and Fracture of Gold-Platinum Polycrystals Strengthened by Spinodal Decomposition

R. W. CARPENTER, *Acta Metall.*, 1967, **15**, (8), 1297-1308

Study of the deformation and fracture characteristics of 60% and 20% Au-Pt, strengthened by spinodal decomposition, shows that both the proportion limit and the work-hardening rate, which is initially higher than normal, increase on isothermal ageing. The proposed theory for the work-hardening behaviour agrees well with the experimental results. Fractures are due to the formation of Pt-rich and Au-rich precipitates in the intergranular regions of the 60% and 20% Au-Pt alloys respectively.

#### Oxidisability of Alloys of Platinum with 2.5 and 8.5% Copper during Heating in Air

E. A. KUZNETSOV and D. V. IGNATOV, *Zh. Neorg. Khim.*, 1967, **12**, (6), 1463-1465

Samples of 2.5 and 8.5% Cu-Pt sheet were heated at 100°C intervals up to 600°C and electron diffraction tests showed the nature of the oxidation film. CuO was detected at 300°C and above. Traces of CuFe<sub>2</sub>O<sub>4</sub> were detected at 500°C for

2.5% Cu-Pt and at 600°C for both alloys. No oxidation was detected at 100 or 200°C.

### **The Effect of the Occlusion of Hydrogen on the Characteristic Temperature of Palladium and the Vibration Amplitudes of its Atoms**

E. A. OWEN and E. W. EVANS, *Br. J. Appl. Phys.*, 1967, **18**, (5), 605-609

Measurement of the fall in intensity of reflection of X-rays with increasing temperature in gas-free pure Pd gives a characteristic temperature of ~267°K compared to 270 and 275°K by specific heat and electrical conductivity methods. The characteristic temperature of Pd rises to 311°K with 0.7 at.% H<sub>2</sub> content. The r.m.s. displacement of Pd atoms at room temperature falls from 0.131 Å for gas-free Pd to 0.113 Å for Pd containing 0.7 at.% H<sub>2</sub>.

### **Comparison of Hydrogen and Deuterium Solubility in Palladium-rich Alloys. Gold-Palladium**

A. MAELAND and T. B. FLANAGAN, *J. Phys. Chem.*, 1967, **71**, (6), 1950-1952

Plots of electrolytic absorption of D<sub>2</sub> in a series of Pd-Au alloys were similar to those obtained for H<sub>2</sub> except for a reduced potential for D<sub>2</sub> in the two-phase system. Equilibrium solubilities of the two isotopes were similar. ΔG and ΔH for the reaction was found to be increasingly negative with increased metal content in the two-phase region.

### **The Effect of Plastic Deformation on the Resistivity and Hall Effect of Copper-Palladium and Gold-Palladium Alloys**

M. J. KIM and W. F. FLANAGAN, *Acta Metall.*, 1967, **15**, (5), 735-745

Electrical resistivity, measured as a function of composition and deformation for 25, 40, 65 and 95 at.% Pd-Au and quenched 50% Pd-Cu alloys, shows an anomalous decrease in resistivity due to a change in the electronic structure from destruction of short range order. The decrease is continuous for Cu-Pd which has a large short range order. For Au-Pd alloys, the decrease is followed by an increase as the effect of strain-induced defects eventually predominates. The anomalous decrease observed for the Hall effect is described similarly.

### **An Approximate Density of States Curve and its Relation to the Measured Electrical Resistivity of Gold-Palladium Alloys**

*Ibid.*, 747-752

The resistivities of the Au-Pd system, described by a simple two-band model corrected for electron interaction, were measured by the Van der Pauw method at 90, 195, 273, 373, 413 and 473°K. Density of states curves obtained from published values of paramagnetic susceptibilities and electronic specific heat coefficients predict

0.52 holes for Pd as opposed to the calculated value of 0.55.

### **The Recovery Kinetics of Deformed Copper-Palladium and Gold-Palladium Alloys**

*Ibid.*, 753-763

The recovery of a range of deformed Au-Pd and Cu-Pd alloys was studied by isochronal and isothermal annealing. The temperature of the annealing stages, which were similar to those obtained for pure metals, was found to be dependent on alloy composition.

### **Relationships between the Hydrogen Content and Electrical Resistance of Palladium + Silver Alloys**

A. W. CARSON, F. A. LEWIS and W. H. SCHURTER, *Trans. Faraday Soc.*, 1967, **63**, (6), 1447-1452

The relative electrical resistance, R/R<sub>0</sub>, and the temperature coefficient, α, of 10-55 at.% Ag-Pd alloys were measured as a function of H content during the absorption and desorption cycles at 25°C. The rate of decrease of R/R<sub>0</sub> with H/Me, the ratio of H atoms to the combined total of Pd and Ag atoms, increases with increasing silver content. The variation of α with H/Me is described in terms of the α, β phase structure of the alloys.

### **Pressure-Composition Isotherms for the Pd + Ag + H System**

A. W. CARSON and F. A. LEWIS, *Ibid.*, 1453-1457

The pressure-composition isotherms (hydride vapour pressure/(H/Me)) for the absorption of H<sub>2</sub> in 0-55 at.% Ag-Pd electrodes at 25°C exhibit "plateau" regions for alloys containing >30% Ag where the α- and β-phases coexist. A graph of isobaric solubility, (H/Me) against at.% Ag, shows that the solubility of H<sub>2</sub> as a function of the Ag content is dependent on the H pressure at which the solubilities are measured.

### **Mechanical Properties at High Temperatures of Ternary Conducting Alloys on a Silver Base**

N. L. PRAVOVEROV, A. N. BUBYREV and I. M. LOBYNTSEVA, *Metallurg. term. Obrabot. Metal.*, 1967, (2), 36-37

Simultaneous addition of Pd with Cr, Co or Fe greatly increases the mechanical strength of Ag at 20-300°C. Maximum effect occurs with Pd and Fe together; Pd plus Co and Cr gives almost as much effect. 0.4-0.5% Pd + 0.02% of the other metal(s) are the most effective additions.

### **Vaporisation Rates, Vapour Pressures and Heats of Sublimation of Rhenium, Rhodium, Palladium and Titanium**

H. STRASSMAIR and D. STARK, *Z. angew. Phys.*, 1967, **23**, (1), 40-44

Results were obtained by Langmuir's vacuum evaporation method for Rh at 1845-2092°K and

for Pd at 1361–1603°K and these are compared with previous work elsewhere.

### Effects of Mechanical and Thermal Treatment on the Structure and Magnetic Transitions in FeRh

J. M. LOMMEL and J. S. KOUVEL, *J. Appl. Phys.*, 1967, **38**, (3), 1263–1264

Well-annealed bulk FeRh samples exhibit a first-order antiferromagnetic-ferromagnetic transition at 330°K but plastic deformation converts the normal CsCl-type structure to disordered f.c.c. structure, which is only weakly magnetic with no first-order transition. Annealing of the latter at 510°K converts it to highly-ordered CsCl-type structure. The return of the first-order transition occurs in three stages as perfect long-range order is achieved or as defects are annealed out.

### Magnetic Susceptibility and Specific Heat of Nearly Ferromagnetic NiRh Alloys

E. BUCHER, W. F. BRINKMAN, J. P. MAITA and H. J. WILLIAMS, *Phys. Rev. Letters*, 1967, **18**, (25), 1125–1127

Ni<sub>0.63</sub>Rh<sub>0.37</sub> is just on the ferromagnetic side of the critical concentration and has maximum magnetic susceptibility at ~40°K, and an anomalous specific heat below 8°K. The anomaly decreases on either side of this concentration and disappears at Ni<sub>0.55</sub>Rh<sub>0.45</sub> on the paramagnetic side, and at Ni<sub>0.70</sub>Rh<sub>0.30</sub> on the ferromagnetic side. Plots of magnetic susceptibility and  $\gamma$  values of specific heat were plotted against alloy concentration and confirm that 63% Ni is the critical value.

### The Crystal Structure of Hexagonal Rh<sub>2</sub>Al<sub>5</sub>

L.-E. EDSHAMMAR, *Acta Chem. Scand.*, 1967, **21**, (3), 647–651

The structure of arc-melted, hexagonal Rh<sub>2</sub>Al<sub>5</sub>, determined by X-ray powder photography and evaluated using the least squares technique, belongs to the space group P6<sub>3</sub>/mmc and has cell constants  $a=7.893$  and  $c=7.854$  Å. It is compared with the apparently isomorphous Co<sub>2</sub>Al<sub>5</sub> structure.

### The Crystal Structure of IrAl<sub>3</sub>

*Ibid.*, (4), 1104–1105

Single crystal, X-ray powder diffraction studies of IrAl<sub>3</sub> show that it has a DO<sub>18</sub>-type structure and belongs to the space group P6<sub>3</sub>/mmc with cell constants  $a=4.246$  and  $c=7.756$  Å. The Guinier powder pattern data and the interatomic distances are tabulated.

### New Phases in the Vanadium-Iridium System and a Tentative Constitution Diagram

B. C. GIESSEN, P. N. DANGEL and N. J. GRANT, *J. less-common Metals*, 1967, **13**, (1), 62–70

Crystal structures and approximate homogeneity

ranges were established or confirmed for four intermediate phases in the V-Ir system and a tentative constitution diagram is proposed. V<sub>3</sub>Ir and VIr<sub>3</sub> were known previously;  $\alpha$ -VIr and  $\beta$ -(V<sub>1-x</sub>Ir<sub>x</sub>)Ir are new. Atomic volumes are given.

### Measurement of the Specific Magnetic Susceptibility of Osmium between 80 and 1850°K by Means of an Improved Faraday Method

W. D. WEISS and R. KOHLHAAS, *Z. angew. Phys.*, 1967, **22**, (6), 476–481

The specific magnetic susceptibility,  $\chi$ , of pure Os, determined by an electronically compensated microbalance with a relative resolving power of 0.25  $\mu$ g, was found to be 0.068 emu/g at room temperature. The value of  $\chi$  between 80° and 1850°K is given by  $\chi=(\int \Delta K dx)/(2mH_y \delta_{max})$ , where  $m$ =mass of the probe and  $H_y$  is the field component in the  $y$  direction.

## CHEMICAL COMPOUNDS

### Formation of Thin Films of PdO and their Electric Properties

H. OKAMOTO and T. AŌO, *Japan. J. appl. Phys.*, 1967, **6**, (6), 779

Oxidation of evaporated Pd films in air at 973°K for 24 h formed thin PdO films. Electrical conductivity of PdO was measured as a function of temperature at 77–560°K in various atmospheres. It decreased on heat cycling. Energy gap, Hall coefficient and Hall mobility were studied also.

### Phase Relations in the Systems TiO<sub>2</sub>-IrO<sub>2</sub> and SnO<sub>2</sub>-IrO<sub>2</sub> in Air

C. L. MCDANIEL and S. J. SCHNEIDER, *J. Res. N.B.S., Sect. A, Phys. Chem.*, 1967, **71A**, (2), 119–123

X-ray diffraction studies of the pseudobinary systems TiO<sub>2</sub>-IrO<sub>2</sub> and SnO<sub>2</sub>-IrO<sub>2</sub> after treatment in air for 18 h at 800, 900 and 1000°C indicated similar phase diagrams with no intermediate phases. Maximum solid solution of TiO<sub>2</sub> occurs with 5 mol.% IrO<sub>2</sub> at 1040°C. Solid solution of TiO<sub>2</sub> in IrO<sub>2</sub> extends to 12 mol.% TiO<sub>2</sub> at 1040°C, the dissociation temperature. Limited solid solubility of SnO<sub>2</sub> in IrO<sub>2</sub> exists to 3 mol.% SnO<sub>2</sub> at 1025°C, the dissociation temperature. Solid solution in SnO<sub>2</sub> was not detected up to 1400°C.

### Thermal Dissociation of Iridium Trichloride

N. I. KOLBIN and V. M. SAMOILOV, *Zh. neorg. Khim.*, 1967, **12**, (7), 1747–1750

Investigations during the thermal dissociation of  $\beta$ -IrCl<sub>3</sub> and of mixed  $\alpha$ - and  $\beta$ -IrCl<sub>3</sub> at 810–1040°K showed that no mono- $\beta$  or dichloride of Ir coexists in these conditions. During the formation of IrCl<sub>3</sub> from its elements  $\Delta H^\circ_{298.15} = -242.0 \pm 6.0$  kJ/mole,  $\Delta S^\circ_{298.15} = -242.0 \pm 8.0$

J/°K. mole. For solid  $\text{IrCl}_3$ ,  $S_{298.15}^\circ = 127.0$  J/°K. mole. The dissociation pressure is 1 atm at 1036°K.

**Carbon Disulphide, Carbonyl Sulphide, and Alkyl and Aryl Isothiocyanate and Perfluorothioacetone Complexes of Nickel, Palladium, Platinum, Rhodium, and Iridium**  
M. C. BAIRD and G. WILKINSON, *J. Chem. Soc., A, inorg. phys. theor.*, 1967, (6), 865-872

$\text{CS}_2$  reacts with  $\text{Ph}_3\text{P}$  complexes of Ni, Pd, Pt, Rh and Ir in zero or +1 oxidation states to form complexes with the  $\text{CS}_2$  ligand  $\pi$ -bonded, e.g.  $(\text{Ph}_3\text{P})_2\text{PtCS}_2$ . Structurally-related  $\pi$ -complexes occur with COS and alkyl and aryl isothiocyanates although the allyl isothiocyanate-Pt complex is best formed otherwise. Isothiocyanates react with  $(\text{Ph}_3\text{P})_2\text{RhCl}$  to form both  $\pi$ -bonded and donor co-ordinated complexes.  $\text{Pt}(\text{PPh}_3)_3$  reacts with 2,2,4,4-tetrakis(trifluoromethyl)-1,3-dithietan and benzyl chloride to form  $(\text{Ph}_3\text{P})_2\text{Pt}(\text{C}_2\text{F}_6\text{CS})$  and  $(\text{Ph}_3\text{P})_2\text{PtCl}(\text{COPh})$  respectively.  $\text{RhCl}_3(\text{p-FC}_6\text{H}_4\text{N}_2)(\text{PPh}_3)_2 \cdot 0.5\text{CHCl}_3$  is described.

### Tris(triphenylphosphine)rhodium(I) Complexes

W. KEIM, *J. organometall. Chem.*, 1967, 8, (3), P25-P26

Synthesis of  $\sigma$ -bonded Rh(I) complexes containing a Rh-C bond, i.e. methyltris(triphenylphosphine)rhodium and phenyltris(triphenylphosphine)rhodium, and of hydrotris(triphenylphosphine)rhodium are described. The compounds, characterised by IR and NMR, are all air-sensitive, soluble in aromatic solvents and decompose when heated to 150°-200°C.

### On the Polymorphism of Osmium Tetrachloride

P. MACHMER, *Chem. Commun.*, 1967, (12), 610

Elemental analysis, X-ray powder diffractometry and magnetic measurements indicate the existence of two forms of  $\text{OsCl}_4$ . A dark brown chloride, obtained from  $\text{OsO}_4$  and  $\text{SOCl}_2$ , appears to have a cubic lattice constant,  $a = 9.95 \text{ \AA}$ . It is paramagnetic and has a temperature dependent susceptibility.  $\chi_{\text{mole}} = +880 \times 10^{-6}$  c.g.s. units. The black form, synthesised from its elements, can be represented by an orthorhombic unit cell with constants  $a = 12.08$ ,  $b = 11.96$ , and  $c = 11.68 \text{ \AA}$ . It is also paramagnetic but has a temperature-independent susceptibility of  $+1080 \times 10^{-6}$  c.g.s. units.

## ELECTROCHEMISTRY

### Contribution to the Electrolytic Polishing of Platinum

J. TOUŠEK, *Coll. Czech. chem. Commun.*, 1967, 32, (6), 2348-2352.

When a Pt electrode is immersed in a  $\text{H}_2\text{SO}_4$ /

$\text{HNO}_3$  mixture and a.c. is applied it dissolves fairly quickly, the rate of solution increasing with  $\text{H}_2\text{SO}_4$  concentration, but this tendency is limited by the easy formation of a passive oxide film which is difficult to reduce. Pt foil samples were produced by electrolytic polishing in a bath of equal volumes of 96%  $\text{H}_2\text{SO}_4$ , 65%  $\text{HNO}_3$  and 80%  $\text{H}_3\text{PO}_4$ . The rate of polishing at 0.5 A/cm<sup>2</sup> was about  $3.10 \cdot 10^{-6}$  g.cm<sup>-2</sup>s<sup>-1</sup>.

### Anodic Oxidation of Ethylene on Noble Metals and Alloys. Parametric and Isotopic Examination of Mechanisms

A. T. KUHN, H. WROBLOWA and J. O'M. BOCKRIS, *Trans. Faraday Soc.*, 1967, 63, (6), 1458-1467

The anodic oxidation of  $\text{C}_2\text{H}_4$  on the platinum group metals, Au, Ag, Hg and on the alloys Pd-Au, Rh-Pd, Cu-Rh, Cu-Au, Pt-Rh and Pt-Ni was determined in aqueous and deuterated electrolytes at 80°C. An estimate of the isotopic effect and several reaction mechanisms are suggested. The graph of rate of oxidation/heat of sublimation of substrate is described in terms of variable rates and rate determining steps. The treatment indicates why Pt is the superior electrocatalyst.

### Structure and Catalytic Activity of Platinised Platinum

D. F. A. KOCH, *Extended Abstr., 131st Nat'l Mtg., Electrochem. Soc.*, 1967, (May), abstr. 174

Studies on platinised Pt electrodes show that the surface area of Pt measured by  $\text{H}_2$  adsorption increases with increasing weight of Pt deposited, indicating that pore areas are included in the determination, whereas capacitance measurements are confined to surface reactions. A decrease in Pt deposition potential results in a decrease in surface area of Pt deposited as the  $\text{H}_2$  coverage is increased, which inhibits nucleation and results in an increase in particle size. Catalytic activity below 0.5 V is  $\propto$  surface area obtained by  $\text{H}_2$  adsorption; at 0.67 V it is  $\propto$  area determined by capacitance measurements, i.e. purely a surface reaction.

### Structural Studies of Porous Electrodes

E. Y. WEISSMAN, *J. Electrochem. Soc.*, 1967, 114, (7), 658-665

Non-destructive measurements, used to determine surface area, porosity, pore size distribution, microporosity and polarisation curves of Pt black-Teflon-Ta screen electrodes, show that the micropores in the radii range 25-200 Å determine the performance. The structural geometry of the electrode was investigated with reference to electrochemical activity and can be represented by the equation  $i = a \exp(bS)$ , where  $i$  = current density,  $S$  = surface area,  $a$  and  $b$  are constants depending upon the electrode and the experimental conditions.

### Gold-Palladium Electrocatalysts

J. H. FISHMAN and M. YARISH, *Electrochim. Acta*, 1967, 12, (5), 579-581

Homogeneous Au-Pd alloys containing 30-40% Au and 60-80% Au show significant changes in bulk characteristics due to d-band filling effect. The correlation between this effect and their catalytic properties is shown in the H<sub>2</sub>-O<sub>2</sub> oxidation reaction for which there is a maximum activity at 30% Au, falling off rapidly and approaching zero at ~70% Au. Addition of Au to a Pd-H electrode in the presence of CO decreases the polarisation to a minimum at 40% Au; above 40% Au polarisation increases, indicating that the presence of Au increases resistance to CO poisoning.

### Pretreatment of Pt-Au and Pd-Au Alloy Electrodes in the Study of Oxygen Reduction

A. DAMJANOVIC and V. BRUSIĆ, *J. electroanal. Chem. interfacial Electrochem.*, 1967, 15, (1), 29-33

The effect of pretreatment of Pt-Au and Pd-Au electrodes in the form of wires sealed into a glass tube or threaded through a small Teflon cylinder were studied during O<sub>2</sub>-reduction. 5% Au-Pt has the same V/log i relationship whether treated chemically or thermally whereas electrochemical pretreatment gives a high activity for the reduction. Similar behaviour is observed for 80% Au-Pt; electrochemical pretreatment produces behaviour similar to that of pure Pt; thermal and chemical treatment produces behaviour similar to that of Au. The effect of thermal pretreatment of kinetics is discussed and the results are rationalised in terms of alloy composition and structure.

### Studies on the Electrochemistry of Osmium

J. LLOPIS and M. VÁZQUEZ, *Anal. R. Soc. Esp. Fis. Quim., Ser. B, Quim.*, 1967, 63, (3), 273-281

Studies of the polarisation curves and anodic and cathodic charging curves of Os, electrodeposited on Pt from neutral solutions of Na<sub>2</sub>[OsCl<sub>6</sub>], show that anodic surface oxidation leads to Os films being formed more than one molecule thick. In HClO<sub>4</sub> electrolytes Os is oxidised to soluble OsO<sub>4</sub> at 0.83 V; a similar effect is observed in HCl solution together with Cl<sub>2</sub> evolution. OsO<sub>4</sub><sup>2-</sup> has been identified in alkaline electrolytes.

## ELECTRODEPOSITION AND SURFACE COATINGS

### An Apparatus for Heavy Rhodium Plating

A. E. YANIV, *Plating*, 1967, 54, (6), 721

Bright and smooth Rh deposits on silver-plated brass electrical contacts were obtained at 50°C, 1 A/dm<sup>2</sup> to a thickness of 10 μ in H<sub>2</sub>SO<sub>4</sub> solution, after cleansing and activation. A jolting device prevented adhesion of bubbles. Abrasion tests

showed the high wear-resistance of contacts plated in this manner. The anode of the plating bath was platinised Ti expanded sheet.

## LABORATORY APPARATUS AND TECHNIQUE

### Criteria of Soil Aggressiveness towards Buried Metals. I. Experimental Methods

G. H. BOOTH, A. W. COOPER, P. M. COOPER and D. S. WAKERLEY, *Br. corros. J.*, 1967, 2, (3), 104-108

The redox potential, E<sub>H</sub> at pH=7, as a factor in the aggressiveness of soil towards buried metals, was measured using a solid stemmed probe with duplicate Pt electrodes in the tip in conjunction with a saturated calomel reference electrode inserted in the soil 1 ft away from the probe. The mean potential of the duplicate electrodes,  $\bar{E}$ , was used to calculate E<sub>M</sub> using relationship, E<sub>H</sub> =  $\bar{E}$  + 0.250 + 0.060 [pH - 7].

### Air Depolarised Electrolytic Oxygen Generator

R. A. WYNVEEN and K. M. MONTGOMERY, *J. Electrochem. Soc.*, 1967, 114, (6), 589-592

O<sub>2</sub> in ambient air is separated from N<sub>2</sub> and inert gases by reacting it at a cell cathode with simultaneous evolution of pure O<sub>2</sub> at the anode. Both electrodes are Ni grids with a uniform surface layer of Pt black mixed with Teflon and the electrolyte is KOH solution. Performance depends on inlet air flow and pressure, and on moisture balance between H<sub>2</sub>O content of the air and the electrolyte vapour pressure.

## HETEROGENEOUS CATALYSIS

### The Problem of the Size of Platinum Losses in Nitric Acid Production

H. SIKORA and E. BLASIAK, *Przem. Chem.*, 1967, 46, (4), 199-200

The principal factors involved in the loss of Pt in HNO<sub>3</sub> production and some proposed improvements are discussed.

### Formation of PtO<sub>2</sub> - the Source of Platinum Losses in Nitric Acid Production

H. SIKORA, J. KUBICKI and E. BLASIAK, *Ibid.*, (5), 257-258

The loss of Pt in HNO<sub>3</sub> manufacture is now believed to be due to the evolution of PtO<sub>2</sub> rather than to evaporation of Pt. Its capture by CaO is effected by formation of a compound of the type xCaO.yPtO<sub>2</sub>, where x and y may equal 1. This assumes that an essential step in the oxidation of ammonia is Pt ⇌ PtO<sub>2</sub>.

### Study of a Pilot Unit for Catalytic Reforming

P. MAURET, A. KLEIN, J.-L. ABATUT and H. ROQUES, *Chim. Ind., Gén. chim.*, 1967, 97, (10), 1650-1658  
A pilot unit for the automation and optimisation

of catalytic Pt reforming using a digital computer has been set up at Institut National des Sciences Appliquées, Toulouse. Incorporated are sensors developed to continuously measure octane number, catalyst activity, as well as chromatographic analysis. Reported are first results of control techniques and of mathematical models applied to the problem.

### Development of a Mathematical Description of Platforming for Optimisation of the Process. II.

YU. M. KHOROV, G. M. PANCHENKOV, YU. A. TIRAK'YAN, S. P. ZEL'TSER and F. R. FRADKIN, *Kinetika i Kataliz*, 1967, 8, (3), 658-662

The differential form of the mathematical description of Platforming is independent of the dimensions of the reactors. Optimum conditions were established by finding the limiting points from the mathematical relations.

### Structure and Activity of Noble Metal Alloy Catalysts. I. The Activity of Supported Rh-Pt Alloy Catalyst in the Hydrogenation of Aromatic Compounds

K. YOSHIDA, *Nippon Kagaku Zasshi*, 1967, 88, (2), 125-129, A9

The activity per unit wt. of alloy of supported, homogeneous Rh-Pt in the hydrogenation of  $C_6H_6$ ,  $C_6H_5OH$  and  $C_6H_5COOH$  is shown to be a function of the alloy composition and has a maximum value of 20-40% Rh-Pt. Results indicate that activity is dependent on electronic structure of the alloy and is independent of the reactant.

### II. State of Dispersion of Metal on the Supported Rh-Pt Alloy Catalyst

*Ibid.*, 220-222, A14

Determination of the total surface area of catalyst, support and free metal for Rh-Pt dispersed on carbon black or activated charcoal by  $N_2$  and CO adsorption at 77°K and 293°K, respectively, indicates that the catalyst is located in islands of several atomic layers on the carriers. This agrees well with X-ray diffraction data.

### III. Activity and Magnetic Susceptibility of Rh-Pt Alloy Catalysts

*Ibid.*, 222-224, A14

Atomic susceptibility values of Rh-Pt alloys, measured with a Faraday balance at 25°C, follow the same pattern as their activities in hydrogenation of aromatic compounds, indicating that activity is due to unpaired *d*-electrons of the alloys.

### IV. The Role Played by Oxygen in the Action of Rh-Pt Alloy Catalyst in the Hydrogenation of Benzoic Acid

*Ibid.*, (3), 292-295

A study of the gradual deactivation of Rh-Pt catalyst during the hydrogenation of aromatic

compounds and its reactivation on contact with air indicates that adsorbed  $O_2$ , which appears to increase the number of unpaired *d*-electrons of the catalyst metal, is necessary to maintain high activity.

### V. Decrease in Activity of Rh-Pt Alloy Catalyst in the Hydrogenation of Benzoic Acid

K. YOSHIDA, T. OTAKI and S. KOIKE, *Ibid.*, 295-298

The decrease in activity of Rh-Pt catalyst during the hydrogenation of  $C_6H_5COOH$  is shown to be due to the toxicity of metal ions in acid anhydrides from the reactor and impurities in the  $C_6H_5COOH$ . A relationship between molecular size and poisoning strength is discussed. X-ray diffraction studies indicate that crystalline growth is too small to be responsible for the observed decrease in activity.

### Nylon-Platinum Catalysts with Unusual Geometric and Selective Characteristics

D. P. HARRISON and H. F. RASE, *Ind. Engng Chem., Fund.*, 1967, 6, (2), 161-169

Catalysts prepared from  $H_2PtCl_6$  and Nylons 66, 6 and 610 showed similar characteristics for  $C_6H_6$  hydrogenation and produced substantial amounts of the intermediate cyclohexene. Nylon 3-Pt became active at a higher temperature and only cyclohexane was produced. Nomex-Nylon-Pt was inactive. These differences are suggested as being due to an arrangement of Pt atoms corresponding to the position of amide groups in the nylon crystal. Apparent interaction between Pt and the amide groups increases the efficiency of Pt compared to catalysts on inert supports.

### The Activity of Nylon-Platinum Hydrogenation Catalysts as Determined by the Structure of Various Nylon Carriers

D. P. HARRISON, *Diss. Abstr. B*, 1967, 27, (8), 2691

The isolation of cyclohexene over some of the catalysts in the hydrogenation of  $C_6H_6$  over Nylon 66, 610, 6, 3 or Nomex impregnated with  $H_2PtCl_6$  was explained by proposing a two point  $C_6H_6$  adsorption on the catalyst surface as supported by kinetic evidence. Cyclohexene is not obtained using any other Pt catalyst with similar physical characteristics. The Pt-amide interaction between catalyst and carrier could not be confirmed due to insufficient sensitivity of apparatus.

### Growth of Single Crystals of Cadmium Chromium Selenide by Liquid Transport with Platinum Catalyst

H. VON PHILLIPSBORN, *J. Appl. Phys.*, 1967, 38, (3), 955-956

Pills of CdSe and  $CrCl_3$  in close contact were heated at ~700°C for three days in a Pt boat. Perfect octahedral single crystals of  $CdCr_2Se_4$

grew in the CdSe by liquid transport, catalysed by Pt.

#### Use of Atomic Absorption Spectrophotometry for the Study of Liquid-phase Adsorption Kinetics

J.-M. VERGNAUD, B. REY-COQUAIS, B. BUATHIER and R. NEYBON, *Bull. Soc. chim. Fr.*, 1967, (6), 2194-2196

An atomic absorption spectrophotometer coupled to a reaction vessel, giving a response time of  $\sim 1$  sec was used to study the liquid-phase adsorption kinetics of Pt/C or Pt/Al<sub>2</sub>O<sub>3</sub>. Initial adsorption rate and the adsorption limit could be measured also.

#### Investigation of Liquid-phase Oxidation of Hydrocarbons on Solid Catalysts. I. Oxidation of Paraffins and Cycloparaffins

N. V. KLIMOVA and I. I. IOFFE, *Kinetika i Kataliz*, 1967, 8, (3), 565-571

The catalytic activity of V<sub>2</sub>O<sub>4</sub>.WO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> can be increased by the addition of Pt and other promoters. A heterogeneous-homogeneous mechanism is assumed for the liquid-phase oxidation of the studied paraffins, cyclo-paraffins and aromatic hydrocarbons. It may be possible to control the process with different combinations of catalysts and inhibitors.

#### Catalytic Properties of Platinum Catalysts. V. Effect of Alkali (KOH) on the Activity of Platinised Carbon

K. H. SCHNABEL, *Ibid.*, 583-591

Small KOH additions increase the activity of Pt/C for C<sub>5</sub>-dehydrocyclisation but larger amounts poison it. Alkali gradually suppresses expansion of the ring in 1,1,3-trimethylcyclopentane. Activation energies for dehydrocyclisation differ significantly with KOH additions. KOH may promote active centres on Pt. Different types of active centre exist on Pt/C with different reactions occurring at each.

#### Hydrogenation of Phenol in the Synthesis of Caprolactam

G. D. LYUBARSKII and M. M. STRELETS, *Khim. Promyshlennost'*, 1967, 43, (7), 481-486

A review of the processes using Ni or Pd catalysts (35 references).

#### On the Negative Effect of Activated Carbon during the Hydrogenation of Unsaturated Compounds on Pt, Ni and Pd Catalysts

D. V. SOKOL'SKII and B. O. ZHUSUNBEKOV, *Zh. fiz. Khim.*, 1967, 41, (5), 1213-1215

Kinetic and potential curves were used to study the effect of mechanical mixtures of activated C with Pt- and Pd-black and Raney Ni catalysts on the H<sub>2</sub> adsorption capacity of unsaturated compounds, C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub>, hept-1-ene and dimethylethynylcarbinol during hydrogenation. The

negative effect of the adsorbent is discussed and the rate of hydrogenation is found to be dependent on the nature of both the catalysts and the unsaturated compound.

#### Relation between Shift of Catalyst Potential and Reaction Rate in Liquid-phase Hydrogenation Processes. IV. Correlation of Activities of Raney Ni, Pt- and Pd-black in Liquid-phase Hydrogenations

V. A. DRUZ' and L. N. SADCHIKOVA, *Kinetika i Kataliz*, 1967, 8, (3), 578-582

Activity of Raney Ni, Pt- and Pd-black were compared in liquid-phase hydrogenations to increase product yields and surface area of each catalyst. Product yield depends on the specificity of the individual catalyst.

#### Hydrogenation of Glucose on Raney Nickel Catalysts. I.

F. B. BIKHANOV, D. V. SOKOL'SKII, N. I. POPOV, N. YA. MALKINA and A. M. KHISAMETDINOV, *Ibid.*, 620-624

Pd or Ru additions to Raney Ni catalysts may increase the activity by 30% for the hydrogenation of glucose under pressure, with intense agitation. Optimum additions are 0.1-0.5% Ru or 5% Pd. Increased stability of the promoted catalysts was not apparent.

#### Catalytic Activity of Reduced Noble Metal-Base Metal Mixed Oxides

G. C. BOND and D. E. WEBSTER, *Chem. Ind.*, 1967, (21, May 27), 878-879

Mixed oxides of Pt and either Fe, Co, Ni or Cu, and of Pd and either Co or Ni, when prepared by Adams' method, have activities in excess of single oxides alone or of mechanically mixed oxides. This effect was shown in hydrogenations of C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub> (6% v/v in CH<sub>3</sub>OH), 2-methylbut-3-yn-2-ol (7.5% v/v in CH<sub>3</sub>OH), and cyclohexene (17% v/v in CH<sub>3</sub>OH) at 30°C, 1 atm H<sub>2</sub>. It is suggested that on reduction of a mixed base metal-noble metal oxide part of the base metal forms a solid solution with the noble metal.

#### Hydrogenation of Dimethylethynylcarbinol on Palladium/Polyacrylonitrile Catalyst

D. V. SOKOL'SKII, O. A. TYURENKOVA and E. I. SELIVERSTOVA, *Zh. fiz. Khim.*, 1967, 41, (6), 1404-1410

The rate of hydrogenation of dimethylethynylcarbinol on Pd/polyacrylonitrile, which is found to increase with increasing amount of catalyst and reactant, is faster in CH<sub>3</sub>OH and C<sub>2</sub>H<sub>5</sub>OH solutions than in aqueous solutions, but the reaction ceases as the catalyst surface becomes significantly charged with H<sub>2</sub>. The hydrogenation is more selective in neutral and alkaline solutions. An increase in acid or alkali concentration re-

duces the rate of reaction and the lateral displacement of the anode potential.

### Catalytic Hydrogenation of Butyronitrile

H. GREENFIELD, *Ind. Engng Chem., Product Res. Dev.*, 1967, **6**, (2), 142-144

Tests with Ni, Co, Pt, Pd, Rh, and Ru catalysts for the hydrogenation of butyronitrile to amines showed that Ni and Co appear to be best for the preparation of the primary amine butylamine, Rh best for production of secondary amine dibutylamine, and Pt and Pd best for production of tertiary amine tributylamine. Resistance to poisoning, the use of  $\text{CH}_3\text{OH}$  or  $\text{H}_2\text{O}$  as solvents and the effects of alkaline additives were studied.

### Kinetics of Electrodeposition and Catalytic Activity of Thin Films of Ruthenium

M. FLEISCHMANN, J. KORYTA and H. R. THIRSK, *Trans. Faraday Soc.*, 1967, **63**, (5), 1261-1268

Current-time curves, used to investigate the electrore crystallisation of Ru from acid  $\text{RuCl}_3$  solutions on to a Hg electrode, show that Ru is deposited in a single layer with a thickness of half the lattice repeat in the  $c_0$  direction (2.136 Å) of a h.c.p. lattice. The catalytic evolution of  $\text{H}_2$  is confined to the edges of the growth centres of Ru and is similar to that exhibited for bulk Pt metals.

### The Catalytic Activities of Rhodium and Ruthenium in the Hydrogenolysis of Ethane. Influence of the Concentrations of Hydrogen and Ethane on the Reaction Rate

G. K. STAROSTENKO, T. A. SLOVOKHOTOVA, A. A. BALANDIN and K. A. EL KHATTIB, *Vest. Moskov. Univ., Ser. II, Khim.*, 1967, (3), 63-67

5% Ru/SiO<sub>2</sub> has much greater specific activity than 5% Rh/SiO<sub>2</sub> for catalysing the hydrogenolysis of  $\text{C}_2\text{H}_6$ . Results of studies of the effects of the partial pressures of  $\text{H}_2$  and  $\text{C}_2\text{H}_6$  on the reaction mechanism are tabulated.

## HOMOGENEOUS CATALYSIS

### Homogeneous Catalysis in the Reactions of Olefinic Substances. VIII. Isomerisation of 1,5-Cyclooctadiene with Dichlorobis(tri-phenylphosphine)platinum(II)

H. A. TAYIM and J. C. BAILAR, *J. Am. Chem. Soc.*, 1967, **89**, (14), 3420-3424

A study of the homogeneous isomerisation of 1,5-cyclooctadiene by  $[\text{PtCl}_2(\text{PPh}_3)_2]$  in the presence of the essential cocatalyst  $\text{SnCl}_4 \cdot 2\text{H}_2\text{O}$  in  $\text{N}_2$  or  $\text{H}_2$  atmosphere is shown to proceed via a stepwise mechanism of hydride addition- abstraction with the formation of 5-coordinate hydridoplatinum-olefin complex. The role of  $\text{SnCl}_4 \cdot 2\text{H}_2\text{O}$  is investigated and is found to function as the ligand  $\text{SnCl}_3^-$  which is a strong  $\pi$ -acceptor and prevents reduction of the Pt(II).

### Homogeneous Hydrogenation of Methyl Linoleate Catalysed by Platinum-Tin Complexes

E. N. FRANKEL, E. A. EMKEN, H. ITATANI and J. C. BAILAR, *J. org. Chem.*, 1967, **32**, (5), 1447-1452

The relative reactivity of catalysts in the homogeneous hydrogenation of methyl linoleate is in the order  $\text{H}_2\text{PtCl}_6 + \text{SnCl}_4 > (\text{PPh}_3\text{As})_2\text{PtCl}_2 + \text{SnCl}_4 > (\text{PPh}_3\text{P})_2\text{PtCl}_2 + \text{SnCl}_4 > (\text{PPh}_3)_3\text{PtOH} + \text{SnCl}_4 > \text{SnCl}_4 - (\text{PPh}_3)_3\text{PtOH}$ . Rate curves for the reactions are given. Conjugated dienetrienes in *trans*, *trans* configuration are the major product except for  $\text{H}_2\text{PtCl}_6$  and  $\text{SnCl}_4$  which gives *trans*-dienes.

### Butadiene from Vinyl Chloride. The Platinum(II)-catalysed Coupling of Vinyl Halides

F. N. JONES, *Ibid.*, 1667-1668

The reductive coupling of vinyl chloride to give butadiene is catalysed by  $(\text{C}_2\text{H}_5)_4\text{NSnCl}_3$  with CsF and  $\text{PtCl}_2$  in aqueous DMF at 25°C. The effects of varying the reaction conditions and the Sn:Pt ratio are evaluated. The formation of an isomer of  $[(\text{SnCl}_3)_2\text{PtCl}_2]^{2-}$  and the role of CsF in the reaction are discussed.

### The Reaction of Rhodium Trichloride with Dienes

K. C. DEWHURST, *J. org. Chem.*, 1967, **32**, (5), 1297-1300

$\text{RhCl}_3$  catalyses the addition to *iso*- $\text{C}_3\text{H}_6$  of  $\text{C}_2\text{H}_5\text{OH}$  to give two isomeric ethers in a ratio which is temperature-dependent. On a larger scale, the air-stable complex  $[(\text{C}_6\text{H}_5)_x\text{RhCl}_2]_{17}$  is formed which gives an oil containing only hydrocarbons after hydrogenation with Rh/C. A similar reaction occurs with butadiene but the oil obtained by hydrogenation of this Rh complex gave a  $\text{C}_{10}$  ether.

### Hydride Transfer Reactions Catalysed by Metal Complexes

H. B. CHARMAN, *J. Chem. Soc., B, phys. org.*, 1967, (6), 629-632

Dehydrogenation of *iso*- $\text{C}_3\text{H}_7\text{OH}$  to  $(\text{CH}_3)_2\text{CO}$  is catalysed homogeneously by  $\text{RhCl}_3$  in the presence of LiCl and concentrated HCl. The mechanism is believed to be abstraction of a hydride ion from the  $\alpha\text{C}$  of *iso*- $\text{C}_3\text{H}_7\text{OH}$  by  $\text{RhCl}_3$  with subsequent transfer of this to the proton of HCl, resulting in evolution of  $\text{H}_2$ , the rate of which decreases as Rh metal is precipitated.

### Organic Syntheses by Means of Noble Metal Compounds. Part 32. Selective Decarbonylation of $\alpha,\beta$ -Unsaturated Aldehydes Using Rhodium Complexes

J. TSUJI and K. OHNO, *Tetrahedron Lett.*, 1967, (23), 2173-2176

The decarbonylation of  $\alpha$ -substituted cinnamaldehydes in the presence of  $\text{ClRh}(\text{PPh}_3)_3$  in  $\text{C}_6\text{H}_6$  or  $\text{CH}_2\text{Cl}_2$  yields mainly *cis*-olefins. A dimeric complex is precipitated with sterically

hindered aldehydes at high temperatures unless organonitrile solvents are used. Acyl and aromatic aldehydes are readily decarbonylated at 200°C or above, in the presence of the complex  $\text{CIRh}(\text{CO})(\text{PPh}_3)_2$  which is a more selective catalyst than  $\text{PdCl}_2$ .

### Reactions and Catalytic Properties of Rhodium Complexes in Solution

B. R. JAMES, *Coord. Chem. Rev.*, 1966, 1, (4), 505-524

The catalysed synthesis of Rh(III) complexes, the hydride, allylic and carbonyl complexes of Rh are reviewed, together with their reactivity as homogeneous catalysts in the hydrogenation and polymerisation of olefins and acetates and isomerisation of olefins. The solution chemistry of Rh is also discussed. (160 references.)

### Catalytic Properties of Platinum Group Metal Phthalocyanines

B. D. BEREZIN and A. V. LOSHCHILOVA, *Kinetika i Kataliz*, 1967, 8, (3), 592-598

Os and Ru phthalocyanines have high catalytic activity but other Pt metal phthalocyanines are inactive.  $(\text{HSO}_4)_2\text{OsPc}$  is more active than  $(\text{HSO}_4)_2\text{RuPc}$ . Both are more active than Fe phthalocyanine. The effects of NaF, HCN and  $\text{NH}_3$  on their reactions were studied. The kinetic equation, rate constants and activation energies of these catalysts were derived from quantitative studies and a mechanism for phthalocyanine catalysis is suggested.

### Catalytic Oxidation of Ethylene to Acetaldehyde in the Presence of Complexes of Ruthenium and Other Platinum Metals

A. M. OSIPOV, K. I. MATVEEV and N. N. SHUL'TS, *Zh. neorg. Khim.*, 1967, 12, (7), 1886-1892

Studies of the oxidation of  $\text{C}_2\text{H}_4$  to  $\text{CH}_3\text{CHO}$  in aqueous solutions of Pt metals and of Au showed that the addition of citric acid and some other oxycarbonic acids considerably increases the activity of Ru(III) chloride complexes, and that in solutions containing Ru(III) complexes, citric acid and Cu(II) salts an intermediate complex of these three is formed. There are similarities between the mechanisms when using Pd(II), Ru(III) or Pt(II) complex catalysts.

## FUEL CELLS

**New Batteries Pack Hefty Doses of Energy**  
*Chem. Engng*, 1967, 74, (14, July 3), 38

Douglas Aircraft Co. has developed a rechargeable aerospace battery with Zn anode, Pt-plated Ni mesh cathode and novel separators. Energy density is 100 w.h/lb, shelf life is two years, and it operates at -40 to +300°F. A 5 A.h model has been cycled 2500 times without loss of capacity. The company has two patented methods for electrode production.

### A Unifying Scheme for the Electrochemical Oxidation of Carbonaceous Fuels on Platinum in Sulphuric Acid

J. A. SHROPSHIRE, *Electrochim. Acta*, 1967, 12, (3), 253-258

A two-site generalised scheme is proposed for the adsorption and oxidation on Pt in aqueous  $\text{H}_2\text{SO}_4$  of the carbonaceous fuels, here represented by  $\text{C}_4\text{H}_{10}$ , HCHO and  $\text{C}_2\text{H}_4$ . The oscillatory potential phenomena, observed during oxidation, are also explained on the basis of a two-site surface.

### Fuel Cell Oxidation of Hydrogen on Movable, Partially Submerged Platinum Anodes

H. J. DAVITT and L. F. ALBRIGHT, *J. Electrochem. Soc.*, 1967, 114, (6), 531-535

Potentiostatic studies of two flat Pt anodes partially immersed in 1 N  $\text{H}_2\text{SO}_4$  at 30°C, 1 atm showed that the electrochemical oxidation of  $\text{H}_2$  is affected by meniscus formation, the electrolyte film formed on the exposed parts of the anodes, the surface roughness, and  $\text{H}_2$  adsorption by exposed Pt.

## CHEMICAL TECHNOLOGY

### Considerations and Experiments for a Critical Evaluation of the Platinised Titanium Anode

E. ZIRNGIEBL, *Chem.-Ing.-Tech.*, 1967, 39, (12), 752-756

Electrochemical comparisons of platinised Ti and graphite electrodes show that  $\text{Cl}_2$  has lower potential on the former and that the anode shape and cell characteristics are also important. Amortisation of a cell with platinised Ti anodes is quicker because of the reduced potential.

### The Kinetics of Metallic Activation Sintering of Tungsten

I. J. TOTH and N. A. LOCKINGTON, *J. less-common Metals*, 1967, 12, (5), 353-365

Small amounts of Pd or Ni powerfully activate the sintering to high density of W and W-2%  $\text{ThO}_2$  when introduced as halide salt solution for impregnation followed by reduction to metal. Optimum amounts, representing monoatomic layer were 0.317 wt.% Pd and 0.130 wt.% Ni for 3.3 $\mu$  W particles.

## GLASS TECHNOLOGY

### Preparation of Optical Quality Glass in Small Batches

A. D. PEARSON, J. R. FISHER and W. R. NORTHOVER, *J. Am. Ceram. Soc.*, 1967, 50, (4), 219-220

A method is described for the preparation of small batches of calcium lithium borate and borosilicate glass free of bubbles, inclusions and striations using a Pt crucible and stirrer.

## TEMPERATURE MEASUREMENT

### Two-Point Comparison

E. W. JONES, *Instrum. Control Syst.*, 1967, **40**, (1), 115-118

A two-point method for testing and calibration of Pt resistance thermometers gives accuracy of  $\sim 0.015^{\circ}\text{C}$  at  $-100^{\circ}\text{C}$  and  $\sim 0.006^{\circ}\text{C}$  at  $500^{\circ}\text{C}$  on the International Practical Temperature Scale.

### A Precision PtRh-Pt Thermocouple for Research and Industry

M. BEDUHN and W. HEYNE, *Feinger. Tech.*, 1967, **16**, (6), 257-260

Three East German research institutes have developed the "Model DAMW" Pt:10% Rh-Pt thermocouple instrument, which is suitable for both industrial and laboratory uses. Its construction, characteristics and calibration are described.

## NEW PATENTS

### METALS AND ALLOYS

#### Heat Treatment of Platinum-Cobalt Magnets

INTERNATIONAL NICKEL LTD.

*British Patent 1,067,054*

Remarkable magnetic properties can be produced in pure alloys containing 19.8-31.2% Co by subjecting them to a disordering treatment at a temperature above  $900^{\circ}\text{C}$  for 30 min to 1 h, cooling to  $630-750^{\circ}\text{C}$  at a rate of  $50-150^{\circ}\text{C}/\text{min}$ , cooling to room temperature, ageing at  $630-700^{\circ}\text{C}$  for 5 min - 2 h and then quenching to room temperature.

#### Tungsten-Ruthenium Alloy

U.S. ATOMIC ENERGY COMMISSION

*British Patent 1,070,114*

The high temperature strength of W can be improved by adding 1.1-12% Ru (based on the weight of the alloy). A preferred composition is 1.1 wt.% Ru and 98.9% W.

#### Alloys for Strain-Gauge Elements

KABUSHIKI KAISHA HITACHI SEISAKUSHO

*U.S. Patents 3,305,815-7*

In strain gauges the strain element consists of a binary alloy of Os with 90-99% Pt (815), a ternary alloy of 20-60 at.% Pt, 20-60 at.% Pd and 5-30 at.% Ir (816) and a ternary alloy of 15-80 at.% Pt, 15-80 at.% Pd and 2-15 at.% Mo.

#### Hydrogen Diffusion Tubes

JOHNSON, MATTHEY & CO. LTD.

*U.S. Patent 3,312,043*

A closing plug for sealing the open end of Pd or Pd-Ag alloy  $\text{H}_2$  diffusion tubes consists of material with approximately the same coefficient of thermal expansion and dimensioned to fit tightly with a projecting, threaded spigot of smaller diameter than the tube and used to form a means for attachment of or for stabilising an internal support for the tube. This corresponds to *British Patent 1,009,326*.

### ELECTROCHEMISTRY

#### Electrode Boiler

IMPERIAL METAL INDUSTRIES (KYNOCHE) LTD.

*British Patent 1,068,732*

An electrode for an electrode boiler, e.g. for boiling  $\text{H}_2\text{O}$ , has the parts immersed in the electrolyte (at least) made of Ti or its alloys coated with Ir, Rh, Ir-Pt, Rh-Pt or Ir-Rh-Pt.

#### Production of Platinum and Palladium Oxides

JOHNSON, MATTHEY & CO. LTD.

*French Patent 1,458,185*

Oxidation of these metals is achieved by electrolysis of a Pt or Pd anode in a bath containing molten  $\text{NaNO}_3$  and an alkali metal halide. This corresponds to *Belgian Patent 664,526*.

### ELECTRODEPOSITION AND SURFACE COATINGS

#### Coating Titanium Surfaces

SOCIETE D'ELECTRO-CHIMIE DES ACIERIES

ELECTRIQUES D'UGINE *British Patent 1,069,005*

Process for coating Ti or its alloys with a metal of the Pt group. The metal to be coated is acid pickled and the Pt group metal deposited and then heated at  $150-300^{\circ}\text{C}$ .

#### Applying Designs to Metallic Bases

JOHNSON MATTHEY & CO. LTD.

*French Patent 1,455,917*

A decorating composition for application to a noble metal base consists of a metallising paste containing Au, Ag, Pt, Pd or alloys thereof.

#### Palladium Plating

JOHNSON, MATTHEY & CO. LTD.

*German Patent 1,239,159*

An aqueous neutral or alkaline Pd bath contains a Pd compound, e.g.  $(\text{PdNH}_3)_2(\text{NO}_2)_2$ , and a  $\text{NH}_4$  salt of a weak acid which does not form an