

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Nanoscale Precipitates and Phase Transformations in a Rapidly-Solidified Fe–Pt–B Amorphous Alloy

D. V. LOUZGUINE-LUZGIN, W. ZHANG and A. INOUE, *J. Alloys Compd.*, 2005, 402, (1–2), 78–83

XRD and calorimetry were used to study the phase transformations on heating of rapidly solidified ($\text{Fe}_{0.75}\text{Pt}_{0.25}\text{B}_{25}$). TEM established the existence of nano-scale cubic cF4 Fe(Pt) solid solution particles within the as-solidified amorphous matrix. The particles of the cF4 Fe(Pt) phase start growing at elevated temperature and undergo ordering to form a tP4 FePt compound followed by the precipitation of a tI12 Fe_2B phase from the residual amorphous matrix.

The High-Pressure Modification of CePtSn – Synthesis, Structure, and Magnetic Properties

J. F. RIECKEN, G. HEYMANN, T. SOLTNER, R.-D. HOFFMANN, H. HUPPERTZ, D. JOHRENDT and R. PÖTTGEN, *Z. Naturforsch.*, 2005, 60b, (8), 821–830

High-pressure (HP) modification of CePtSn was carried out under multianvil high pressure (9.2 GPa) and high temperature (1325 K) conditions from the normal-pressure modification. Both modifications are built up from Pt centred trigonal prisms. Together, the Pt and Sn atoms form different 3D [PtSn] networks in which the Ce atoms fill channels. Susceptibility measurements of HP-CePtSn indicate Curie-Weiss behaviour above 40 K with an experimental magnetic moment of 2.55(1) μ_{B}/Ce atom, indicating trivalent Ce.

Chemical Synthesis and Magnetic Properties of Well-Coupled FePt/Fe Composite Nanotubes

H. L. SU, S. L. TANG, N. J. TANG, R. L. WANG, M. LU and Y. W. DU, *Nanotechnology*, 2005, 16, (10), 2124–2128

Heating a porous Al_2O_3 template loaded with an alcohol solution of a Fe chloride and Pt chloride mixture in flowing H_2 at 670°C gave L1_0 FePt nanotubes (1). FePt/Fe composite nanotubes were then obtained by reducing the alcohol solution of the Fe chloride within (1) at 470°C. For $(\text{FePt})_{100-x}/\text{Fe}_x$ ($x = 0\text{--}26$ at.%), the hard and soft phases were well coupled and the coercivity was tunable over 1.27–2.73 T.

Heats of Displacement of Hydrogen from Palladium by Noble Gases

A. J. GROSZEK, E. LALIK and J. HABER, *Appl. Surf. Sci.*, 2005, 252, (3), 654–659

Noble gases (He, Ne, Ar) produced heat evolution when contacted with Pd powder partially saturated with H. The noble gases displace the adsorbed H species from the Pd surface, causing their reabsorption in the Pd lattice with the exothermic heat of Pd–H bond formation, or the formation of H_2 .

Properties of the Quaternary Amorphous Alloy

$\text{Pd}_{40}\text{Ni}_{40}\text{B}_{10}\text{P}_{10}$

Q. LI, D. GREIG, S. H. KILCOYNE, P. J. HINE, J. A. D. MATTHEW and G. BEAMSON, *Mater. Sci. Eng. A*, 2005, 408, (1–2), 154–157

The title alloy (1) was prepared in bulk form, without the use of B_2O_3 flux, by 50% substitution of B for P in the $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ system. (1) was shown to be largely amorphous by neutron and X-ray diffraction and DSC. The XPS data suggest partial substitution of B for P. With the addition of B, glass-forming ability without any fluxing compound was demonstrated.

Stress Evolution in Sputter-Deposited Fe–Pd Shape-Memory Thin Films

Y. SUGIMURA, I. COHEN-KARNI, P. MCCLUSKEY and J. J. VLASSAK, *J. Mater. Res.*, 2005, 20, (9), 2279–2287

Fe–26–30 at.% Pd films (1) were deposited by magnetron sputtering. (1) are highly supersaturated solid solutions of Pd in Fe with a b.c.c. crystal structure and very fine grain size. (1) undergo an irreversible densification at $> 100^\circ\text{C}$. The high-temperature austenite phase can be retained at low temperature by annealing (1) at 900°C followed by rapid cooling. Depending on the composition of (1), the metastable austenitic phase transforms to either a b.c.t. or a f.c.t. martensite at \sim room temperature. Formation of the f.c.t. martensite is reversible.

Reactive Diffusion between Pd and Sn at Solid-State Temperatures

T. TAKENAKA, M. KAJIHARA, N. KUROKAWA and K. SAKAMOTO, *Mater. Sci. Eng. A*, 2005, 406, (1–2), 134–141

Sn/Pd/Sn diffusion couples (1) were prepared by a diffusion bonding technique. (1) were isothermally annealed between $T = 433$ and 473 K for various times in a silicone oil bath. PdSn_4 , PdSn_3 and PdSn_2 compound layers were observed at $T = 433$ K, but only PdSn_4 and PdSn_3 layers were found at $T = 453$ and 473 K. Volume diffusion was the rate-controlling process of the reactive diffusion between Pd and Sn.

Saturated Solid-Solution Hardening Behavior of Ir–Hf–Nb Refractory Superalloys for Ultra-High Temperature Applications

J. B. SHA and Y. YAMABE-MITARAI, *Ser. Mater.*, 2006, 54, (1), 115–119

In Ir–3Hf– x Nb the solubility limitation of solutes Hf and Nb in the Ir solid solution is close to Ir–3Hf–5Nb (1). (1) has a monolithic saturated f.c.c. structure, and a 0.2% yield strength of 140 MPa, even at 1950°C , compared with 19.7 MPa for pure Ir. A large solid-solution hardening effect is obtained in the Ir alloys, in which the solutes have a large misfit parameter with Ir and a small solubility limitation.

CHEMICAL COMPOUNDS

Solvent-Induced Supramolecular Isomerism in [Pt(S=C(NH₂)₂)₄]²⁺ Croconate Salts

P. A. GALE, M. E. LIGHT and R. QUESADA, *Cbem. Commun.*, 2005, (47), 5864–5866

Slow diffusion of acetone into a 1:1 mixture of tetrakis(thiourea)Pt(II) dichloride and croconic acid disodium salt in DMSO–H₂O gave crystals of [Pt(SC(NH₂)₂)₄][C₅O₅]²⁻·4DMSO (1). (1) forms a 3D H-bonded assembly containing two types of channels that accommodate the solvent molecules. The DMSO molecules within the smaller channels are held by two H bonds; the larger channels contain solvent held by only one H bond.

Reaction of [(C₆H₆)RuCl₂]₂ with 7,8-Benzoquinoline and 8-Hydroxyquinoline

J. G. MALECKI, M. JAWORSKA, R. KRUSZYNSKI and J. KŁAK, *Polyhedron*, 2005, 24, (18), 3012–3021

[(C₆H₆)RuCl₂]₂ was reacted with 7,8-benzoquinoline and 8-hydroxyquinoline in MeOH. The magnetic properties of [Ru(C₆H₆NO)₃]⁺·MeOH (1) relate to the antiferromagnetic coupling of the Ru centres in the crystal lattice. The EPR spectrum of (1) indicates a single isotropic line only, characteristic of Ru³⁺, with spin equal to 1/2.

ELECTROCHEMISTRY

Light-Assisted Synthesis of Pt-Zn Porphyrin Nanocomposites and Their Use for

Electrochemical Detection of Organohalides

W. WIYARATN, S. HRAPOVIC, Y. LIU, W. SURAREUNGCHAI and J. H. T. LUONG, *Anal. Chem.*, 2005, 77, (17), 5742–5749

Pt-Zn porphyrin nanocomposites (1) were synthesised using zinc porphyrin and H₂PtCl₆ in the presence of light and ascorbic acid. The Pt nanoparticles were embedded within the Zn porphyrin matrix. A glassy C electrode was modified with Nafion-stabilised (1) and used for dehalogenation of carbon tetrachloride, chloroform, pentachlorophenol, chlorobenzene and hexachlorobenzene. The modified electrode exhibited catalytic activity for the reduction of the organohalides at –1.0 V vs. Ag/AgCl.

Electrochemical Behaviour of Amorphous and Nanoquasicrystalline Zr–Pd and Zr–Pt Alloys in Different Environments

K. MONDAL, B. S. MURTY and U. K. CHATTERJEE, *Corros. Sci.*, 2005, 47, (11), 2619–2635

Melt spun amorphous and nanoquasicrystalline Zr₇₀Pd₃₀ (1) and Zr₈₀Pt₂₀ (2) alloy ribbons show better corrosion resistance than Zr in all solutions studied. Both are susceptible to chloride attack and pitting has been observed. Complete passivation was observed in H₂SO₄, while gradual breakdown of the passivating layer occurs in NaOH. In general, the nanoquasicrystalline state in (1) and (2) shows better corrosion resistance than the amorphous state.

PHOTOCONVERSION

Red Electrophosphorescence of Conjugated Organoplatinum(II) Polymers Prepared via Direct Metalation of Poly(fluorene-*co*-tetraphenylporphyrin) Copolymers

Q. HOU, Y. ZHANG, F. LI, J. PENG and Y. CAO, *Organometallics*, 2005, 24, (19), 4509–4518

PL decay studies indicated that polyfluorene-*co*-tetraphenylporphyrin Pt(II) (PFO-PtTPP) is a triplet emitter. EL emission from the fluorene segment was completely quenched for copolymers with PtTPP content as low as 0.5 mol%. The external quantum efficiency of ITO/PEDT/PVK/PFO-PtTPP (1 mol%) + PBD (40 wt.%) /Ba/Al was 0.43%.

Single-Layer Electroluminescent Devices and Photoinduced Hydrogen Production from an Ionic Iridium(III) Complex

M. S. LOWRY, J. I. GOLDSMITH, J. D. SLINKER, R. ROHL, R. A. PASCAL, G. G. MALLIARAS and S. BERNHARD, *Cbem. Mater.*, 2005, 17, (23), 5712–5719

[Ir(dF(CF₃)ppy)₂(dtbbpy)](PF₆) (dF(CF₃)ppy = 2-(2,4-difluorophenyl)-5-trifluoromethylpyridine; dtbbpy = 4,4'-di-*tert*-butyl-2,2'-dipyridyl) can be used as a chromophore in single-layer electroluminescent devices and as a photosensitiser for H₂ production. The blue-green electroluminescent emission (500 nm) and relative quantum yield of H₂ (2025 μmol H₂) were at the time of publication the highest values to date.

Synthesis, Characterization and Fabrication of Solar Cells Making Use of [Ru(dcbpy)(tptz)X]X (Where X = Cl⁻, SCN⁻, CN⁻) Complexes

S. ANANDAN, S. LATHA, S. MURUGESAN, J. MADHAVAN, B. MUTHURAMAN and P. MARUTHAMUTHU, *Sol. Energy*, 2005, 79, (5), 440–448

Dye-sensitised TiO₂ solar cells were fabricated using [Ru(dcbpy)(tptz)X]X (dcbpy = 4,4'-dicarboxy-2,2'-bipyridine; tptz = 2,4,6-tris(2-pyridyl)-*s*-triazine; X = Cl⁻, SCN⁻, CN⁻) attached to sol gel processed TiO₂ electrodes. The tptz functions as a spectator ligand, whereas the dcbpy functions as the anchoring ligand with sufficient visible light absorption.

SURFACE COATINGS

Al–Pt MOCVD Coatings for the Protection of Ti6242 Alloy Against Oxidation at Elevated Temperature

M. DELMAS, D. POQUILLON, Y. KIHN and C. VAHLAS, *Surf. Coat. Technol.*, 2005, 200, (5–6), 1413–1417

Al–Pt coatings (1) were obtained by MOCVD using Me₃(MeCp)Pt and AlH₃·N(CH₃)₂(C₂H₅). The isothermal oxidation at 873 K of (1) on Ti6242 coupons was carried out for 90 h. Oxidation kinetics revealed a strong transient oxidation regime followed by a diffusion driven parabolic one. (1) are dense, develop scales composed of γ-Al₂O₃ and δ-Al₂O₃, and they prevent Ti diffusion from the alloy to the surface.

HETEROGENEOUS CATALYSIS

XAFS Characterization of Pt-Fe/Zeolite Catalysts for Preferential Oxidation of CO in Hydrogen Fuel Gases

M. KOTOBUKI, T. SHIDO, M. TADA, H. UCHIDA, H. YAMASHITA, Y. IWASAWA and M. WATANABE, *Catal. Lett.*, 2005, 103, (3–4), 263–269

Pt-Fe/mordenite catalyst (1) showed high activity and selectivity for the oxidation of CO in H₂-rich gas compared with Pt/mordenite. The states of the metallic components in ion-exchanged, H₂ pre-treated and post-PROX samples were studied by XAFS. Pt forms metallic clusters after H₂ pretreatment or the PROX experiment, whereas a large part of the Fe exists as oxides even after H₂ treatment. Preferential CO adsorption onto Pt on (1) was demonstrated.

Characterization and Catalytic Performance of a Bimetallic Pt–Sn/HZSM-5 Catalyst Used in Denitratation of Drinking Water

R. RODRÍGUEZ, C. PFAFF, L. MELO and P. BETANCOURT, *Catal. Today*, 2005, 107–108, 100–105

Pt-Sn/HZSM-5 zeolite (1) was characterised by TPR, H₂ chemisorption, XPS and ¹¹⁹Sn Mössbauer spectroscopy to examine its role during the catalytic reduction of nitrate ions in H₂O (denitratation). These techniques showed a significant decrease in the H:Pt ratio upon Sn addition, Sn surface enrichment, the formation of PtSn alloys and Pt catalysis of the Sn reduction. (1) exhibits high catalytic activity for the reduction of nitrate to form N₂. The role of Sn is to reduce nitrate or nitrite according to a redox process, while the Pt maintains Sn in the metallic state.

Catalytic Activities of Pd-TiO₂ Film Towards the Oxidation of Formic Acid

B. XIE, Y. XIONG, R. CHEN, J. CHEN and P. CAI, *Catal. Commun.*, 2005, 6, (11), 699–704

Pd-TiO₂/ITO films (1) were prepared by a dip-coating and subsequent photodeposition (UV light) procedure. (1) were characterised by XRD, SEM and open circuit voltage. (1) not only exhibited higher photocatalytic and photoelectrocatalytic activities, compared with a TiO₂/ITO film, but also showed non-photocatalytic activity towards HCOOH degradation at room temperature and atmosphere pressure.

Catalytic Properties of Several Supported Pd(II) Complexes for Suzuki Coupling Reactions

O. VASSILYEV, J. CHEN, A. P. PANARELLO and J. G. KHINAST, *Tetrahedron Lett.*, 2005, 46, (40), 6865–6869

Pd(II) complexes with N-ligands were synthesised and tested for the Suzuki coupling reaction. These complexes were also heterogenised on silica. Immobilised dichloro(*N*-(3'-trimethoxysilyl)propyl-1,2-ethanediamine-*N,N'*)-Pd showed high catalytic activity, which makes it a useful system for biaryl compound synthesis. Leaching of the Pd into DMA/H₂O was negligible.

HOMOGENEOUS CATALYSIS

Synthesis, Reaction, and Recycle of Fluorous Palladium Catalysts for an Asymmetric Allylic Alkylation without Using Fluorous Solvents

T. MINO, Y. SATO, A. SAITO, Y. TANAKA, H. SAOTOME, M. SAKAMOTO and T. FUJITA, *J. Org. Chem.*, 2005, 70, (20), 7979–7984

A chiral fluorous aminophosphine (1) bearing two fluorous ponytails was prepared from (*S*)-prolinol and applied to the Pd-catalysed asymmetric allylic alkylation of 1,3-diphenyl-2-propenyl acetate with a dialkyl malonate/*N,O*-bis(trimethylsilyl)acetamide/LiOAc system with ≤ 97% ee. The Pd catalyst formed from (1) and [Pd(η³-C₃H₅)Cl]₂ was easily separated from the reaction mixture and could be reused five times.

Heck and Suzuki Coupling Reactions in Water Using Poly(2-oxazoline)s Functionalized with Palladium Carbene Complexes as Soluble, Amphiphilic Polymer Supports

D. SCHÖNFELDER, O. NUYKEN and R. WEBERSKIRCH, *J. Organomet. Chem.*, 2005, 690, (21–22), 4648–4655

Three amphiphilic, H₂O-soluble diblock copolymers based on 2-oxazoline derivatives with pendant *N*-heterocyclic carbene/Pd catalysts in the hydrophobic block (1) were investigated. (1) in the Heck coupling of iodobenzene with styrene in neat H₂O gave high activities with TOF ≤ 2700 h⁻¹ at 110°C. The Suzuki coupling of phenylboronic acid with iodobenzene and bromoarenes in neat H₂O exhibited even higher catalytic activity with TOF ≤ 5200 h⁻¹ at 80°C.

A Preparative Route to Methyl 3-(Heteroaryl)acrylates Using Heck Methodology

T. J. KWOK and J. A. VIRGILIO, *Org. Process Res. Dev.*, 2005, 9, (5), 694–696

Methyl 3-(heteroaryl)acrylates were prepared using Heck coupling of heteroarene halides with methyl acrylate catalysed by Pd(OAc)₂/P(OCH₃)₃. A 3-fold excess of methyl acrylate and a bromoheteroarene in DMF were heated under N₂ with either triethylamine or diisopropylethylamine. P(OCH₃)₃ and Pd(OAc)₂ were used in a 2:1 ratio with a catalyst loading of 1–5 mol%. The highly volatile P(OCH₃)₃ is readily separated during the removal of the DMF.

Palladium Catalysed Aryl Amination Reactions in Supercritical Carbon Dioxide

C. J. SMITH, M. W. S. TSANG, A. B. HOLMES, R. L. DANHEISER and J. W. TESTER, *Org. Biomol. Chem.*, 2005, 3, (20), 3767–3781

Pd-catalysed C–N bond formation in sc-CO₂ has been achieved. Formation of carbamic acid was avoided by the use of an *N*-silylamine as the coupling partner. The system Pd₂dba₃ (1 mol%) with X-Phos (2 mol%) enabled the catalytic amination of aryl bromides and chlorides with *N*-silylanilines. The methodology was extended to *N*-arylation of *N*-silyldiarylamines, *N*-silylazoles and *N*-silylsulfonamides.

Microwave-Assisted Organic Synthesis: Scale-Up of Palladium-Catalyzed Aminations Using Single-Mode and Multi-Mode Microwave Equipment

K. T. J. LOONES, B. U. W. MAES, G. ROMBOUITS, S. HOSTYN and G. DIELS, *Tetrahedron*, 2005, 61, (43), 10338–10348

Batchwise scale-up of Buchwald-Hartwig aminations under microwave irradiation was investigated. Pd(OAc)₂ was combined with 2-(dicyclohexylphosphanyl)biphenyl or 2-(di-*t*-butylphospanyl)biphenyl. Multi-mode (several vessels irradiated in parallel per batch) as well as single-mode (one vessel irradiated per batch) platforms were successfully used. The single-mode platform is the most convenient since it allows automatic continuous batchwise production.

FUEL CELLS

Optimization of the Sputter-Deposited Platinum Cathode for a Direct Methanol Fuel Cell

K. MAKINO, K. FURUKAWA, K. OKAJIMA and M. SUDOH, *Electrochim. Acta*, 2005, 51, (5), 961–965

Electrodes prepared by sputtering Pt onto C cloths were evaluated as the cathodes (1) for DMFCs. Pt loading below 0.25 mg cm⁻² achieved higher mass activities than a Pt loading of 0.5 mg cm⁻² prepared by the paste method. However, an increase in Pt loading reduced the catalyst activity for the ORR. Pt utilisation efficiency was ~ 10 times higher at a Pt loading of 0.04 mg cm⁻². An optimum addition of Nafion to (1) improved the catalyst activity.

Instability of Pt/C Electrocatalysts in Proton Exchange Membrane Fuel Cells

P. J. FERREIRA, G. J. LA O', Y. SHAO-HORN, D. MORGAN, R. MAKHARIA, S. KOCHA and H. A. GASTEIGER, *J. Electrochem. Soc.*, 2005, 152, (11), A2256–A2271

Equilibrium concentrations of dissolved Pt species from Pt/C electrocatalyst in 0.5 M H₂SO₄ at 80°C increased with applied potential from 0.9 to 1.1 V vs. reversible H electrode. The Pt surface area loss for a short-stack of PEMFCs, operated at open-circuit voltage (~ 0.95 V), was higher than another operated under load (~ 0.75 V). The formation of soluble Pt species (such as Pt²⁺) is claimed to play an important role in Pt surface loss in PEMFC electrodes.

On the Preparation and Stability of Bimetallic PtMo/C Anodes for Proton-Exchange Membrane Fuel Cells

N. P. LEBEDEVA and G. J. M. JANSSEN, *Electrochim. Acta*, 2005, 51, (1), 29–40

Bimetallic PtMo/C (1) electrocatalysts were synthesised via reductive coprecipitation with either formaldehyde or formic acid as reducing agent. The electrochemical behaviour of (1) was characterised by CV in H₂SO₄ solutions as well as in MEAs. (1) were shown to be inherently unstable and to suffer from the gradual loss of Mo due to its dissolution into the electrolyte, regardless of whether the components are well-mixed or present in the segregated phases.

Synthesis of Platinum Nanoparticles and Then Self-Assembly on Nafion Membrane to Give a Catalyst Coated Membrane

H. TANG, Z. LUO, M. PAN, S. P. JIANG and Z. LIU, *J. Chem. Res.*, 2005, (7), 449–451

A catalyst-coated membrane (1) for a PEMFC with Pt loading of 2.8 μg cm⁻² was prepared by self-assembling charged Pt particles at SO₃⁻ groups on the membrane surface. Proton conductivity of (1) was 0.0932 S cm⁻¹. The performance of the self-assembled MEA achieved 2.3 mW cm⁻². This corresponds to Pt utilisation of 821 W per 1 g Pt.

MEDICAL USES

Surface PEGylation and Ligand Exchange Chemistry of FePt Nanoparticles for Biological Applications

R. HONG, N. O. FISCHER, T. EMRICK and V. M. ROTELLO, *Chem. Mater.*, 2005, 17, (18), 4617–4621

By covering magnetic FePt nanoparticles (1) with PEGylated thiol and dopamine ligands, H₂O-soluble (1) of great stability were synthesised. The surface thiol ligands are readily exchanged with other thiols bearing chain-end functionalities. The surface binding of both DNA and protein to (1) was achieved.

Tumour-Inhibiting Platinum(II) Complexes with Aminoalcohol Ligands: Biologically Important Transformations Studied by Micellar Electrokinetic Chromatography, Nuclear Magnetic Resonance Spectroscopy and Mass Spectrometry

P. SCHLUGA, C. G. HARTINGER, M. GALANSKI, K. MEELICH, A. R. TIMERBAEV and B. K. KEPPLER, *Analyst*, 2005, 130, (10), 1383–1389

(*SP*-4-2)-Bis[(R)-(-)-2-aminobutanol-κN]dichloroPt(II) and (*SP*-4-2)-bis[(R)-(-)-2-aminobutanolato-κ²N,O]Pt(II) (1) exhibit a strongly pH-dependent rate of reaction with guanosine 5'-monophosphate. NMR confirmed the existence of equilibrium between the ring-opened and ring-closed species. An appreciable increase in binding in the presence of sodium dodecyl sulfate (SDS) micelles was explained in terms of the activation of (1). There is a shifting of the equilibrium towards the ring-opened species, induced by adduct formation between SDS and (1).

Precipitation Hardening of a Cu-Free Au–Ag–Pd–In Dental Alloy

H.-J. SEOL, K.-H. SON, C.-H. YU, Y. H. KWON and H.-I. KIM, *J. Alloys Compd.*, 2005, 402, (1–2), 130–135

Three phases were observed in the solution-treated title alloy (1): (a) Au–Ag based phase with small amounts of In and Pd as matrix; (b) InPd phase as particle-like structures; and (c) Pd-rich phase as lamellar precipitates. By ageing (1), the very fine Pd-rich intergranular precipitates grew toward the grain interior as a lamellar structure, and finally the coarsened Pd-rich precipitates covered a large part of the Au–Ag based matrix.