

Potential Applications of Fission Platinoids in Industry

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Amounts of fission-generated platinoids, as recovered from high-level liquid radioactive wastes, could considerably supplement amounts of metals claimed from natural sources. Of particular interest are fission palladium and rhodium, which can be decontaminated from other fission products to a non-hazardous level. What remains is intrinsic radioactivity which is weak in fission palladium, and which in fission rhodium decays to an acceptable level after 30 years. The intrinsic radioactivity should not play a negative role when fission platinoids are applied to nuclear technology. Some non-nuclear applications of fission platinoids may be possible, if irradiation and contamination of personnel as well as uncontrolled release of the platinoids, are avoided.

The potential utilisation of fission-produced platinum metals (fission platinoids, FPs) as valuable products has attracted attention in the last few decades, as large amounts of spent nuclear fuel have accumulated worldwide. One metric ton of spent fuel, at a burn up of 33 GWd/t (gigawatt days per metric ton) contains > 1 kg palladium (Pd), > 400 g rhodium (Rh) and > 2 kg ruthenium (Ru) (1). Indeed, by 2030 spent nuclear fuel could supply up to 1000 t Pd and 340 t Rh. This would be a considerable addition to the yield from natural sources.

FPs can be isolated from radioactive wastes that originate in the reprocessing of spent fuel by the Purex process. The FPs are contained mainly in the solid residue left after the dissolution of the fuel at an early processing stage, and in the aqueous waste stream emerging from the first process cycle (high-level liquid waste). Processes for the recovery of FPs from both fractions have been developed worldwide (2).

The purification of FPs during recovery can be so effective that the radioactivity of the fission products left is compatible with safety regulations. However, there remains the intrinsic radioactivity

of the isolated FPs. Fission Pd contains 17 wt.% of the radioactive isotope ^{107}Pd (half-life $t_{1/2} = 7 \times 10^6$ years). Besides, fission Pd only contains stable isotopes with atomic masses 104 (17 wt.%), 105 (29 wt.%), 106 (21 wt.%), 108 (12 wt.%) and 110 (4 wt.%). ^{107}Pd is a soft beta emitter (maximum energy, $E_{\text{max}} = 0.035$ MeV), but the radiation intensity at the surface of a foil of fission Pd metal (0.2 mg cm^{-2}) is 520 Bq cm^{-2} (3) and this is higher than permitted by safety regulations in most countries. The specific beta radioactivity was compiled as 1.7×10^6 Bq g^{-1} (1), while 2.6×10^6 Bq g^{-1} was found experimentally (3).

The intrinsic radioactivity of fission Rh and Ru may be a more serious problem. Fission Rh consists almost exclusively of the stable isotope ^{103}Rh and trace mass fractions of the isotopes ^{102}Rh ($t_{1/2} = 2.9$ years) and $^{102\text{m}}\text{Rh}$ ($t_{1/2} = 207$ days). Electron capture is the exclusive decay mode of ^{102}Rh and it is the main decay mode of $^{102\text{m}}\text{Rh}$, which also is a beta and positron emitter and undergoes an internal transition. The gamma radiation of the isotopes is rather energetic (0.47 to 1.1 MeV). Radioactive decay can reduce the radioactivity to an acceptable level after a suitable, indeed long storage time (≥ 30

years). The specific radioactivity of isolated Rh after a 5 year storage is $\sim 10^7$ Bq g⁻¹ (1).

Fission Ru exhibits higher intrinsic radioactivity than Rh, caused by the isotopes ¹⁰³Ru (0.0036 wt.%, $t_{1/2} = 39$ days) and ¹⁰⁶Ru (3.8 wt.%, $t_{1/2} = 1.02$ years). ¹⁰³Ru emits beta particles with $E_{\max} = 0.76$ MeV and little gamma radiation (0.05–0.61 MeV), and decays to stable ¹⁰³Rh. ¹⁰⁶Ru is a soft beta emitter ($E_{\max} = 0.039$ MeV), which is in equilibrium with ¹⁰⁶Rh ($t_{1/2} = 30$ seconds), a hard beta emitter ($E_{\max} = 3.54$ MeV), also releasing some gamma radiation (0.51–0.62 MeV). The stable isotopes are ⁹⁹Ru (2.4 × 10⁻⁴ wt.%), ¹⁰⁰Ru (4.2 wt.%), ¹⁰¹Ru and ¹⁰²Ru (both 34 wt.%), and ¹⁰⁴Ru (24 wt.%). The specific radioactivity of isolated Ru after 5 year and 20 year storage has been compiled as 3 × 10¹¹ and 1 × 10⁷ Bq g⁻¹, respectively (1).

It is clear that intrinsic radioactivity restricts the applicability of isolated FPs. It has been suggested that the radioactive isotopes should be removed either by current methods of isotope separation or by special methods. Atomic vapour laser (4) and plasma (5) separation processes are applicable to all three FPs, laser separation to remove ¹⁰⁷Pd from fission Pd (6) and electromagnetic separation to remove radioactive isotopes from fission Ru (7). However, all these operations would inevitably increase the price of isolated FPs which might not be acceptable by the market.

In another approach (8), only stable isotopes of Pd and Rh would be obtained as final products if fission Ru was the exclusively separated platinoid, that is: beta decay of ¹⁰⁶Ru via ¹⁰⁶Rh would give stable ¹⁰⁶Pd, while stable ¹⁰³Rh would be formed from ¹⁰³Ru. However, this would, of course, essentially reduce the yield of FPs; large amounts of Pd and Rh would be left unexploited in the radioactive waste.

Of the three FPs, Pd and Rh are most applicable. Fission Ru is too radioactive, due to the high ¹⁰⁶Ru content, while Ru obtained from natural sources has a lower commercial value than either Pd or Rh.

The intrinsic radioactivity of FPs does not restrict their applications in fields in which it is not in conflict with safety regulations, for example, in nuclear engineering. In other fields, two require-

ments must preferably be fulfilled:

- Irradiation and contamination of personnel must be avoided and,
- uncontrolled release of the FPs' radioactivity must be suppressed to well below the legally permitted level.

The first requirement is fulfilled without special precautions in using fission Pd; the major part of its soft beta radiation is self-absorbed in Pd itself or in its solid support. The range of the radiation in air is 0.2 cm, and is < 0.002 cm in tissue which is considerably shorter than the thickness of the horny layer of human skin. Fulfilling the second requirement differs from application to application.

One precaution is inevitable both in nuclear and non-nuclear applications. Substances containing FPs would have to be treated as radioactive materials in common operations, such as fabrication, refabrication, regeneration and disposal. Such operations would have to be made in correspondingly licensed and equipped facilities and respect safety regulations. However, the impact of this on total productions costs would not necessarily be of great importance.

This review outlines the potential for industrial and small scale applications of FPs. It shows that in some applications the intrinsic radioactivity would play no role, or a subordinate role. Elsewhere the use of FPs could be made compatible with safety regulations, but would not be always practicable. Due to the critical attitude of the public toward nuclear technology and applications, FPs could not be used in the production of consumer goods, even if their role in the production process was indirect and contamination of the final product excluded. On the other hand, the FPs may well be used in the fabrication of products for industrial use. Applications that are not acceptable are medical uses such as the production of bactericidal and antitumour pharmaceuticals, surgical implants, medical equipment and jewellery.

Nuclear Technology

In any applications in this field the intrinsic radioactivity of FPs would play only a minor role. Possible applications are shown below, excluding

“cold” nuclear fusion which, although having promised to be a revolutionary source of energy, turned out to be a misinterpretation of experimental results.

Structural and Special Materials

Areas where platinoid additives improve the properties of structural materials:

- In the Canadian deuterium-uranium reactor (CANDU), pressure tubes made from a Zr-Nb alloy are in contact with heavy water coolant (580 K, 11.1 MPa) on the inner side and with CO₂ coolant on the outer side. Elemental deuterium formed in corrosion reactions diffuses towards the outer side of the tubes and weakens them due to hydrogen embrittlement. To inhibit this, the concentration of deuterium is suppressed by oxidation below the dissociation pressure of Zr hydride. Pd coating catalyses the oxidation, as shown in model experiments with pure Zr and hydrogen (9). Associated problems, such as oxygen corrosion of Zircaloy, catalyst deactivation, neutron absorption by Pd and radioactive waste production were shown to be manageable (10).
- A Pd layer on nickel or cobalt-based alloys and stainless steels catalyses the reaction of hydrogen with oxygen or hydrogen peroxide in water at > 150°C. This lowers the corrosion potential of these materials in pressurised water nuclear reactors (11). A platinoid catalyses the recombination of hydrogen and oxygen in a gas stream and, simultaneously, the decomposition of hydrogen peroxide in a water stream, when the streams are in counter-current contact (12).
- Embrittlement of Zircaloy cladding of oxide fuel rods by fission product cadmium is prevented by Pd (0.25–2.0 g kg⁻¹). The Pd can be blended with the bulk of the fuel, dispersed as coating on the oxide particles before or after their pressing to pellets, or applied as a coating on the inner side of the cladding tubes (13).
- The oxidation resistance of the Zircaloy-4 cladding of fuel elements is increased by alloying its surface with Pd. For example, a Pd layer (2 μm) is electroplated onto the Zircaloy-4 surface and annealed at 950°C and < 10⁻⁴ Pa (14).
- ⁶⁰Co-embedded oxide scales are formed on the

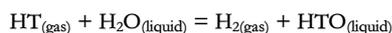
surface of stainless steel in boiling water reactors. The formation is reduced by a thin surface film of Pd, deposited either by vacuum evaporation or electrolysis (15).

- Pd can be a component of shape memory alloys, that is, materials acquiring a prescribed form when heated to transformation temperature and restored to their initial shape on cooling. Such alloys may be TiNiPd, sputter-deposited as a thin amorphous film and crystallised at 700–750°C (16) and Ti₅₀Pd_{50-x}Ni_x, especially when improved by thermomechanical treatment (17). Shape memory alloys can be used in passive safety systems, thermocouplings for pipes and electric drives, equipment for repair and assembly of units, thermomechanical drivers, dampers, flow rate regulators, thermodetectors, self-operating emergency systems, units and elements in electrical transmission lines and electric contact devices (18).
- The Ti-0.2Pd alloy is a prospective material for the construction of containers for solid high-level radioactive wastes, which are to be disposed in a rock salt depository. The passive layers of the material are adequately resistant to gamma radiation when it is in contact with salt brine (19).

Removal of Hydrogen Isotopes from Gases and Liquids

Platinoid catalysed reactions can be of importance in gaseous, liquid and solid phases:

- Tritium, free or bound in tritiated hydrocarbons, is removed from the off-gas stream of a fission reactor by conversion to tritiated water or its mixture with CO₂. Catalysed by Pd, Rh or their mixture deposited on alumina or silica, the reaction proceeds at 90–500°C and atmospheric pressure (20).
- Tritium is removed from the aqueous effluents of a nuclear plant and directed into an aqueous concentrate in combining the electrolysis of tritiated water with the catalysed isotopic exchange reaction:



Deposited on a styrene-divinylbenzene copolymer, Pd catalyses the exchange less efficiently than

Pt, but it can be used in mixture with Pt (21, 22). The catalyst is prepared by agglomeration, crushing the agglomerate, pressing it into a cake and cutting catalyst particles from the cake (22).

- Hydrogen in the primary cooling circuit of a gas-cooled nuclear power reactor is separated from radioactive impurities if it is passed through a Pd alloy film. The cooling gas must be pressurised and free from moisture and oxygen (23, 24).
- To prepare a catalyst for hydrogen/oxygen recombination in a nuclear power plant, a platinoid is deposited on a porous metal, and heated at 400–850°C, when it diffuses into the carrier surface where it forms an alloy layer (25). Alternatively, a ceramic granular material can be coated with Pd and used in a passive catalytic module, which is incorporated in a nuclear reactor for hydrogen mitigation during a core-melt accident (26, 27).
- Alumina beads carrying 0.5% Pd catalyse the H₂/O₂ recombination to 99% at 25°C in compacted solid radioactive waste stored in sealed packages. Hydrogen is formed if the waste is humid and swells as a result of the corrosion of aluminium, steel and zinc (28).

Hydrogen Isotope Diffusion, Trapping and Cleanup

The utilisation of platinoids in the above operations finds broad application in non-nuclear industry (see later section on [Hydrogen Production](#)). Pure Pd metal, but not Pd alloys, exhibits considerable adsorption and permeation capacity for hydrogen; the capacity decreases in the order: Pd > Pd₉₅Co₅ > Pd₉₀Co₁₀ > Pd₉₅U₅ > Pd₃U (300–600 K, ≤ 50 bar) (29).

Hydrogen isotopes are separated from other components of the gas output of a fusion reactor by permeation through Pd-Ag (75/25 wt./wt.) membranes at 350–450°C. The isotopic effects are H₂/D₂ = 1.72 and H₂/DT = 2.06. The Pd-Ag alloy is poisoned by tritiated methane, but is regenerated by heating in air (30). Efficient devices have been constructed and tested in the U.S.A. (Savannah River Site) (31), Russia (32) and Japan (Japan Atomic Energy Research Institute) (33, 34). The dimension and operating conditions of a per-

meator can be calculated by mathematical modelling (35).

Other materials used in permeation membranes are Pd alloys containing 10–40 wt.% Ag, 5–25 wt.% Au, 10–20 wt.% Pt or 5–10 wt.% Rh. Very promising materials are Pd-Ag or Pd-Au alloys with additions of Pt, Rh, Ru or Ir. Pd alloyed with 25 wt.% Ag, Au and Ru exhibits excellent hydrogen permeability and mechanical properties, and is also resistant to hydrogen embrittlement and swelling and fractures caused by helium bubble formation (36). Other applicable Pd alloys, developed for non-nuclear industry, contain 10–30% Ag, 0.5–5% Au, ≤ 2% Y, 0.2–2% Ru, ≤ 1% Pt and 0.01–0.5% Al (37).

The methane poisoning is avoided in a double-function membrane reactor which incorporates a Pd-Ag tube packed in a Ni catalyst bed. After the bulk of HT in the inlet gas is oxidised to HTO over a Pt catalyst, He is added, and the gas is contacted with the Ni catalyst which converts the HTO and CH₂T₂ into HT, CO and CO₂ at 310–600°C. A HT product and a He + CO + CO₂ waste stream are obtained (38–40). A mathematical model accounts for coupled effects of transport-limited permeation of H isotopes and various chemical reactions (41).

Tritium can be separated from liquid Li in a thermonuclear power plant by transfer through a niobium “window” into a helium stream at 980°C. The Nb “window” is protected from oxygen attack on the He side by an electrolytically deposited Pd layer (0.001 cm). Diffusion of Pd into Nb is prevented by an intermediate layer (250 nm) of yttrium which does not form solid solutions with Nb (42). Diffusion through a double-layer Zr-Pd window also separates tritium from liquid Li, and also from Li alloys (for example, Li₁₇Pb₈₃). Li or its alloy flows on the Zr side of the window, and a purge stream of argon and oxygen flows on the side of the Pd coating. At 450°C tritium diffuses rapidly through the window and is recovered as T₂O. Problems like reaction at the Pd surface and corrosion deserve attention (43).

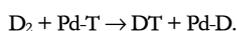
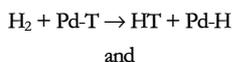
Hydrogen isotopes can be removed from fission and fusion liquid coolants by “pumping” against a partial-pressure drop. A gas containing H

isotopes as impurities is kept in a vacuum (10^{-8} Pa) or a reducing atmosphere on the lower concentration side, and H isotopes are permeated through a Pd or Pd-Ag (75/25) diaphragm (44) or a Pd-coated Zr membrane (45) into an oxidising atmosphere on the higher concentration side. There they are oxidised to water (600–700 K, upstream pressure 0.0007–0.03 Pa). The mechanism is discussed in (46).

The behaviour of tritium on a Pd-Ag (75/25) cathodic membrane with and without a Pd black deposit, that is, the amount of diffused and trapped tritium, the retrodiffusion, diffusion coefficient, tritium concentrations in the alloy sublayer and the diffusion layer thickness, all depend upon the applied cathodic potential, temperature, Pd-Ag membrane thickness, presence of Pd black deposits and time. Without a Pd black deposit, the double layer capacitance is $40 \mu\text{F cm}^{-2}$ and the apparent diffusion coefficient is $3 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ at $\sim 20^\circ\text{C}$. A Pd black deposit increases the diffusion coefficient to $3 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$ (47).

Separation of Hydrogen Isotopes

This separation is based on isotope exchange reactions in Pd, such as:



The separation factors are:

$$\ln \alpha_{\text{HT}} = 284/T + 0.03$$

and

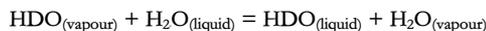
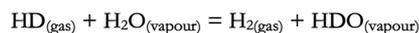
$$\ln \alpha_{\text{DT}} = 114/T + 0.002,$$

that is, at 296 K, $\alpha_{\text{HT}} = 2.69$ and $\alpha_{\text{DT}} = 1.47$ (48), while the ranges $\alpha_{\text{HT}} = 2.68\text{--}4.16$ and $\alpha_{\text{DT}} = 1.47\text{--}1.54$ are given elsewhere (49). Pelletised Pd black can be used at 0°C , and the separation factors depend on the starting H_2/D_2 , H_2/T_2 , and D_2/T_2 ratios (50) and on the temperature (-80 to 100°C) (50, 51) (see also (52)).

Chromatography is currently used to separate H isotopes. The adsorbent can be Pd deposited on alumina (51, 53) and on carbon and other supports in frontal and displacement chromatography (51), and in twin-bed periodic counter-current flow (54). Alternatively, spongy Pd black is used in displacement chromatography (55) and Pd on

kieselguhr has been used in a pilot plant and a production facility constructed in the U.S.A. (Savannah River Plant) (56, 57). Pd can also be carried by a sulfonic acid cation exchanger (58). Problems arising from volume changes of Pd adsorbents are avoided if they are in the form of moulded granules containing a binder. The absorption rate is determined by surface reactions at -78°C but mainly by hydrogen diffusion in pores of the adsorbent at 0°C . Counter-current contact of the gas phase with the adsorbent is preferably achieved by intermittent opening of independent column sections for the gas flow (see (48) and references therein).

Adsorbents consisting of Pd or Rh on alumina, kieselguhr or other suitable oxide can be covered by a lipophilic layer (silicon resin, teflon, etc.), which is permeable to hydrogen gas and water vapour but not to liquid water. Then the isotope exchange reactions are (59):



Other Nuclear Applications

Dissolution of pulverised UO_2 pellets in 8 M HNO_3 at 80°C (a modified head-end operation in the Purex process) is accelerated if they contain 0.1–1.0 wt.% Ru, Rh or Pd. The platinoid is added as RuO_2 , Rh_2O_3 or PdO to UO_2 powder in the fabrication of the pellets, which are sintered at 1750°C in hydrogen (60).

Hydrogen Production

Platinoid-containing membranes are utilised in non-nuclear industry for the separation of hydrogen from other gases. Negligible amounts of FPs might be released to gaseous products from compact metallic or glassy materials. The stability of FPs dispersed as coatings on ceramic or oxide materials would have to be checked in each case. The mechanical properties and the plasticity of Pd-containing membranes can be improved when they are repeatedly loaded with hydrogen, and then unloaded (isobarically or isothermally) (61).

Membranes made from Pd alloys containing 10–30 % Ag, 0.5–5% Au, $\leq 2\%$ Y, 0.2–2% Ru, \leq

1% Pt and 0.01–0.5% Al (B-X alloys) have been applied on industrial scale in the production of hydrogen from ammonia purge gas (37). Pd alloy membranes containing 6–8 wt.% In and 0.5–1.0 wt.% Ru can be used for purification of hydrogen at 400–900°C and 5–10 atm (62).

A Pd-Ag alloy can be spread on a thin film of γ -alumina, which is supported by a porous ceramic hollow fibre (63), or the alloy or Pd can be deposited electrochemically on a fine metal fabric (20–80 μm thread and 5–20 μm mesh) (64). A Pd/porous-glass membrane (65) and a γ -alumina membrane impregnated with Pd in its bulk volume (66) separate hydrogen from nitrogen and carbon monoxide.

Catalysis

In this much used application the platinumoids are mostly contained in closed systems and, if FPs are used, the risk of personnel irradiation and contamination can be minimised. Release of the FPs to the product of the catalysed reaction can be minimised by the catalyst preparation, and minimum losses of the platinumoid components are, in any case, strived for to achieve long catalyst lifetimes. Thus, in some systems the application of FPs could be quite acceptable. Incidentally, the use of an intrinsically radioactive element (technetium) has already been suggested: it strongly increases the catalytic activity of Pd (67).

However, using FPs in automobile catalysts would not be acceptable. The release to the environment, even if minimised, would be worthy of consideration, due to the broad utilisation of such catalysts. Data on Pt concentrations in dust, soil and sediments, biological material and natural waters has been published (68).

The following examples give a value to the possible extent of platinumoid release from a catalyst, and also illustrate the extent of handling the weakly radioactive FPs if they are used as catalyst components.

The lowest release of platinumoids can be expected from compact metal bodies or layers. For example, Pd-Ru alloys (80–90/5–20 w/w) are used as foils covered on one or both sides by a porous copper layer (69). A Pd/Pt/Rh alloy is shaped to a composite wire, containing in its body a fibre of a

Rh/Y alloy; this is braided into a net (70). Another example is a package in which nets from two different alloys (Pd/Rh/Ru/Pt and Pd/Pt/Au) are alternately layered (71). A film of Pd can be supported by a layer of a siloxane polymer on a porous copper membrane (72). Catalysts of the type PdZnTe_{0.2}, PdZn, or PdZn₂ are prepared by reduction with formaldehyde or by metal displacement (73).

A not-so-low release of platinumoids might occur from catalysts in which platinumoids are deposited on porous pretreated oxides: most frequently γ -Al₂O₃, less frequently TiO₂, ZrO₂, SiO₂, V₂O₅ or MoO₃. They are used either without mechanical support, or on a ceramic support such as cordierite. The pretreatment of γ -Al₂O₃ consists of calcining in air at 200°C (74) or 550°C (75, 76), after eventual ball milling in 0.5 M nitric acid (75), or contacting with an (NH₄)₂SeO₃ solution and drying at 50°C (76). Zr(IV) hydroxide can be converted to a superacid by treatment with an (NH₄)₂MoO₄ solution, drying at 110°C and calcining at 600°C (77).

The pretreated oxides (mentioned in the previous paragraph) are contacted with an aqueous solution of H₂PdCl₄, Pd(NO₃)₂ or RhCl₃ at room temperature, dried at 50–120°C and heated in air to 400°C (74, 75, 77) or 540°C (76). The Pd(II) is then reduced to metal by hydrogen at atmospheric pressure and 200°C (77) or 400°C (74), and the Rh(III) is reduced to metal at 0.1 MPa and 500°C (75).

In a wet sol-gel process, Al₂O₃ sol, for example, is formed by reacting Al isopropoxide with hexylene glycol at 120°C. A Rh(III) solution hydrolyses the sol at 85°C to a gel, which is then aged at 80°C, dried at reduced pressure and heated to 600°C in an atmosphere of air or nitrogen (78).

Again calcination is the usual final step of the catalyst preparation if zeolites of various types and ionic forms (79, 80), mordenite (81) and silicon nitride (82) are used as carriers for platinumoids. A non-calcined catalyst with encapsulated dicarbonyl rhodium(I) is prepared by introducing Rh(III) into zeolite Y by ion exchange with Na(I) and heating in a CO atmosphere at 120°C and 1 MPa (83).

On sulfide carriers, Pd or Rh in a valency state > 0 is bound to S atoms. For example, the reaction of bis(2-ethoxyethylxanthato)palladium(II) or

tris(2-ethoxyethylxanthato)rhodium(III) with molybdenyl dithiocarbamate at 430°C and 6.9 kPa in a hydrogen atmosphere results in the take up of Pd or Rh into highly dispersed molybdenum sulfide (84).

Charcoal granules can be loaded with Rh(III) from an aqueous chloride solution, and the Rh(III) is converted to an oxide at 220°C and reduced to a metal crystallite by humidified hydrogen at 325°C (85). An iron/graphite carrier is loaded with Pd(II) from a solution of $(\pi\text{-C}_3\text{H}_5\text{PdCl})_2$ or $\pi\text{-C}_3\text{H}_5\text{PdP}(\text{C}_6\text{H}_5)_3$ in benzene and subsequently calcined in air at 750–850°C (86).

An organic carrier, the styrene-divinylbenzene copolymer HP20, is loaded with Pd from a Pd(II) acetate solution. The Pd(II) is reduced by hydrogen at 100°C and the obtained catalyst is soaked with trichlorobenzene or trimethylbenzene (87).

To prepare a silicon carrier, silica gel is treated with dimethylethoxysilane or triethoxy(2-ethyl-3-pyridyl)silane and propylamine, or by (dimethylethoxysilylmethyl)diphenylphosphine. A silicon polymer is formed on the surface which, if contacted with an aqueous solution of PdCl₂, incorporates Pd(II) bound to a nitrogen or a phosphorus donor atoms (88).

A polymeric support can also be based on silane, silicone or carbon fluoride (89), and a porous material carrying a platinoid can be coated by a layer of a carbon fluoride polymer which is permeable only to gases (90).

Electrochemical Technology

In this area the release of FPs and risks for personnel are reduced if the FPs are contained in compact and corrosion-resistant parts of the equipment involved. These FPs can be applied to the production of dimensionally stable anodes, cathodes for hydrogen evolution, platinised titanium electrodes as diffusion electrodes, three-dimensional electrodes (91), electrodes for fuel cells, monocrystalline electrodes and micro-electrodes in microsensors for organics.

Examples of electrode manufacturing show the extent of manipulation with FPs, and examples of the corrosion rate and the lifetimes give a figure for the FPs expected to be released.

Anodes for electrolytic reactions, made from amorphous alloys Rh-B (75/25), Rh-B-P (70/20/10) and Rh-B-Ti (60/20/20) are representative of compact electrodes. Their corrosion rate in chlorine evolution from aqueous chloride solutions is as low as 0.04–0.07 $\mu\text{m}/\text{year}$ at 200 mA cm^{-2} , 1.2 V vs. SCE and 60–80°C (92). Electrodes made from amorphous alloys, such as Pd_{76-x}Pt_xSi₁₈Cu₆, need no activation treatment (93).

Platinoid Layer/Ti Support Electrodes

Electrodes consisting of a compact support carrying a platinoid-containing layer are more typical. In these cases Ti is often chosen as the support material. It is treated as follows:

- It is electrolytically coated with the FeSn₂ alloy, immersed in a nitrate solution of Pd, Fe and Cd, and heated to 600°C. An active layer 0.04 cm thick is formed, containing 33–36% Pd. The lifetime of such an anode, used to electrodeposit Zn from a 1 M H₂SO₄ + 1 M ZnSO₄ solution, is 255–287 days at 50 mA cm^{-2} , 1.6 V and 35 °C (94).
- A pre-etched Ti coupon is repeatedly wetted with a solution of RuCl₃, PdCl₂, Ti(C₄H₉O)₄ and HCl in butanol, dried at 120°C and heated to 500°C. This forms an active layer in which Pd oxide is finely dispersed in a solid solution of Ru and Ti oxides, containing 22–55 mol% Ru, 0.2–22 mol% Pd and 44–78 mol% Ti. The active layer can be top-coated with a porous layer of Ta₂O₅, formed by applying a solution of TaCl₅ in pentanol and heating to 525°C. The lifetime of the electrode is 140 hours in 1.5 M H₂SO₄ at 50°C and the anode current density is 7.5 kA m^{-2} . In a hypochlorite generator the electrode operated 24 days in diluted brine at a chloride current efficiency of 80–85% (95).
- Ti is mechanically polished and etched by 0.2 M oxalic acid. Then it is repeatedly wetted with a solution of RuCl₃, SnCl₂ and HCl, then dried at 50°C and heated to 350°C (450°C after the last cycle). A RuO₂/SnO₂ layer is formed, the composition of which is controlled by adjusting the concentration of the components in the applied solution. At a Ru content of 30 mass%, its maximum lifetime as an anode in 0.5 M H₂SO₄ at 500 mA cm^{-2} and 30°C is ~12 h (96).

Fuel Cell Catalyst Electrodes

A catalyst electrode for a fuel cell is fabricated by forming a monoatomic layer of Pd or Rh on gold crystallites (5–10 nm in diameter) carried by carbon particles. The metals are underpotential deposited from 1–10 M NaOH or KOH containing 10^{-4} – 10^{-5} M Pd or Rh (97).

Another catalytic electrode is prepared by depositing Pd onto a sputter-etched silicon surface. A 13.5 MHz radio frequency voltage can be used in an argon atmosphere (0.018 torr) both for the sputtering (500 W r.f. power input into the resulting Ar gas discharge, 30 s) and the Pd deposition (50 W, 5 s) (98).

Electrical Technology and Electronics

The potential acceptability of FPs in this field is similar to that in the area of electrochemical technology. Examples of applications are:

- Superconductivity is exhibited at < 2 K by Cr-Ru alloys containing > 17 at.% Ru (99), and has been predicted to be a property of the compound LiPdH_x (100). Ru, Pd and Rh not only enhance the superconducting transition temperature of high temperature superconductors but, for example, also shorten the synthesis of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ from 60 to 10 hours, at a temperature of 880°C instead of at 920 – 950°C (101).
- The compound Al_2Ru is a semiconductor at low temperature, exhibiting rather anomalous direct current conductivities of ~ 10 and $0.21 \Omega^{-1} \text{cm}^{-1}$ at 300 and 0.46 K, respectively (102).
- The Pd-Ag alloy (70/30 w/w) does not react with the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ superconductor at 980 and 1100°C . A foil of the alloy can thus serve as a conductive barrier between the superconductor and a substrate (103). A non-porous, ductile and shiny coating of a Pd-Ag alloy can be deposited electrolytically from a solution containing $\text{PdCl}_2(\text{NH}_3)_2$ or $\text{Pd}(\text{NO}_3)_2(\text{NH}_3)_2$, AgNO_3 , ammonium acetate or ammonium phosphate plus boric acid and mercaptosuccinic acid or mercaptopropionic acid plus succinic acid monoamide (104).
- A Pd coating with increased microhardness can be deposited from a solution containing $\text{PdCl}_2(\text{NH}_3)_4$, ammonium sulfate and a complex of ZnCl_2 with

1,3,6,8-tetraazatricyclo(4,4,1,13,8)dodecane (105), or from a solution containing the salt $(\text{RH})_2\text{PdCl}_4$ (R = tetramethylethylenetetramine) and ammonium sulfate (106).

- Polypyridine complexes of $\text{Ru}(\text{NCS})_2$ and RuCl_2 are used as sensitizers in solar energy conversion cells based on TiO_2 mesoporous electrodes (107).

Further special applications are molecular superconductors based on platinumoid complexes with organic ligands, photoelectrochemical cells, microwave components, thin film resistors, thermocouples, multilayer structures and superthin wire for IC-chips, amorphous soft magnetic recording materials, magnetic and photorecording materials, antiferromagnetic corrosion-resistant films, and sandwich cermet capacitors.

Production of Corrosion Resistant Materials

In this field as well, the FPs would be incorporated in a solid phase and control of their release should thus be possible. Uses may include:

- Up to a few per cent of Pd improves or, depending upon the steel composition and type, causes deterioration to the corrosion resistance of stainless steels in diluted sulfuric acid (108, 109) and in solutions of hydrochloric acid or ferric chloride (110). Pd can suppress a particular form of hydrogen embrittlement (“flaking”) of even low alloy steels, and it can also improve mechanical properties (109). Platinumoids enhance the corrosion resistance of alloys by modifying the cathodic reaction (“cathodically modified alloys”) (111).
- Addition of $\leq 5\%$ Pd enhances the resistance of chromium stainless steels to high-temperature water that contains hydrogen (112), to pressurised superheated steam at 1200°C (109), to $\geq 90\%$ sulfuric acid at $\leq 220^\circ\text{C}$ (113) and to air oxidation at 500°C (114) and 900°C (115). A content of ≤ 0.7 wt.% Rh improves the stability of chromium stainless steel toward sulfuric and nitric acids (116) and ≤ 0.3 wt.% Ru enhances the resistance of the ferritic Fe-40Cr alloy to diluted sulfuric acid (117). Laser surface alloying enhances the resistance to 0.5 M HCl by forming a surface layer of fine cellular dendrites containing 52 wt.% Ru (118). Passive films have been characterised in 0.5 M HCl at

0–0.2 wt.% Pd (119), and in 0.5 M H₂SO₄ and 0.5 M HCl at 0.1–0.2 wt.% Ru (120).

- Steel 316 containing 0.5 wt.% Pd is passivated to 1 N H₂SO₄ by a single cycle of hot pressing and sintering (121). A cathodic alloying additive of Pd ($\leq 0.5\%$) improves the resistance of Cr and Ti alloys in non-oxidising acids or reducing media and also, depending on which components are present, improves the resistance of multicomponent stainless steels in aggressive environments (122).

- Addition of 0.15% Pd or coating with PdO/TiO₂ enhances the resistance of Ti in boiling non-acidic NaCl and MgCl₂ solutions (123). Mo-Cr alloys are resistant to inorganic and organic acids if they contain ≤ 10 wt.% Pd or Ru (124). Promising corrosion resistance in air is exhibited by alloys Al₄₇Ru₅₃, Al₄₈Ru₅₁Y, Al_{44.5}Ru_{50.5}Cr₅ and Al_{44.3}Ru_{50.2}Cr₅B_{0.5} at 1100°C and by alloys Al₄₆Ru₅₂Sc₂ and Al₄₃Ru₅₂Sc₅ at 1350°C (125). Ti metal or Ti-based alloys are resistant to acid chloride brines, if they contain 0.1% Ru (126).

Surface alloying of a Pd plated Ti alloy is achieved by bombarding with Xe ions which disperse Pd homogeneously in the surface layer. This suppresses corrosion in boiling 1 N H₂SO₄ (127). The mechanism of the beneficial effect of Pd on the oxidation resistance of Mo-W-Cr alloys to air and oxygen at 1000–1250°C is elucidated in (128).

Miscellaneous Applications

A metallic and a carbon-containing material can be joined if a Pd/Si brazing material and an active metal (Ti, Zr, etc.) or hydride are placed between the surfaces and heated in vacuum (129). Pd can be a component of high temperature strain gauge alloys, such as Au-Pd-Cr, Au-Pd-Cr-Ni, Au-Pd-Cr-Pt-Al or Au-Pd-Cr-Pt-Fe-Al-Y (130). Other potential applications are hydrogen getters in vacuum cryogenics, cryogenic temperature sensitive elements and crucible materials for growing crystals at superhigh temperatures.

Conclusions

[1] Although fission platinoids (FPs) separated from high-level radioactive wastes will have residual radioactivity, this need not be an insuperable

barrier to their industrial use in particular cases.

[2] A wide range of applications where the use of FPs might be possible has been identified. This includes applications in the nuclear industry, where the materials involved are themselves radioactive or become radioactive during operation, and other applications where the impact of the residual radioactivity could be satisfactorily controlled.

[3] Any industrial utilisation of FPs must meet the following general criteria:

- The cost of separating, processing and using the FPs should not exceed the costs of using naturally derived platinum group metals.
- Irradiation and contamination of personnel as well as uncontrolled release of the FPs into the environment must be avoided.
- It must be ensured that recycling of platinum group metals, which frequently occurs in industry, does not result in the contamination of the general stock of the metals by the weakly radioactive FPs. Especially, any risk of introducing the FPs into materials which later can be used in medicine or jewellery must be excluded. It has to be assessed whether this could be guaranteed by common safety regulations for the treatment of radioactive materials (which in many countries have become very strict in recent decades) or whether additional safeguards must be introduced by authorities and efficiently established by the industry.

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