Kirk-Othmer Encyclopedia of Chemical Technology.

PLATINUM-GROUP METALS

The platinum-group metals (PGMs), which consist of six elements in Groups 8– 10 (VIII) of the Periodic Table, are often found collectively in nature. They are ruthenium, Ru; rhodium, Rh; and palladium, Pd, atomic numbers 44 to 46, and osmium, Os; iridium, Ir; and platinum, Pt, atomic numbers 76 to 78. Corresponding members of each triad have similar properties, eg, palladium and platinum are both ductile metals and form active catalysts. Rhodium and iridium are both characterized by resistance to oxidation and chemical attack (see Platinum-group metals, compounds).

The PGMs are of significant technological importance. They are also extremely rare, owing in part to low natural abundance and in part to the complex processes required for extraction and refining. Unlike gold (see Gold and gold compounds), the majority of which is used for jewelry and investment purposes, the PGMs are used primarily in industrial applications.

One of the earliest recorded uses of platinum was the primitive jewelry articles found in the Esmereldas region of Ecuador (1), which date from several centuries before the Spanish conquest of South America. It is thought that pre-Colombian natives collected platinum nuggets from streams and made primitive articles of platinum or a crude platinum–gold alloy. Archaeological evidence suggests that the jewelry was made by an early form of powder metallurgy, in which small grains of platinum were mixed with gold dust, and heated to build up an homogeneous mixture (see Metallurgy).

Platinum was found in conjunction with gold after the Spanish conquest of South America. It was referred to as platina, or little silver. It was regarded as an unwanted impurity in the silver and gold, and was often discarded. However, scientific interest in platinum gradually grew and in 1741 the first samples of New World platinum were brought to England for scientific examination.

At the start of the nineteenth century, platinum was refined in a scientific manner by William Hyde Wollaston, resulting in the successful production of malleable platinum on a commercial scale. During the course of the analytical work, Wollaston discovered palladium, rhodium, iridium, and osmium. Ruthenium was not discovered until 1844, when work was conducted on the composition of platinum ores from the Ural Mountains.

The records of Faraday, Davy, and those who followed in developing knowledge of electricity show how often platinum was employed to provide a means of carrying, making, and breaking a current. The development of the electric telegraph, the incandescent lamp, and the thermionic valve all involved the use of platinum. Similarly, early internal combustion engines required platinum in the igniter tubes and magnetocontacts. In the late twentieth century, the single most widely developed application of platinum is as a catalyst in a range of chemical processes and petroleum refining, emission control systems, and in fuel cells (qv). Although industrial applications of the other five platinum-group metals came later than those of platinum itself, these too have become widely established in chemical, electrical, and electronic engineering. The most widely used unit of mass for the PGMs is the troy ounce (1 troy oz = 0.0311 kg). However, herein masses are given in metric tons.

Table 1. CAS Numbers and Relative Abundances of Stable Isotopes of PGMs

Isotope	CAS Registry Number	Abundance, %
ruthenium	[7440 – 18 – 8]	
^{96}Ru	[15128 – 32 – 2]	5.52
^{98}Ru	[18393 – 13 – 0]	1.88
^{99}Ru	[15411 – 62 – 8]	12.7
^{100}Ru	[14914 – 60 – 4]	12.6
^{101}Ru	[14914 – 61 – 5]	17.0
^{102}Ru	[14914 – 62 – 6]	31.6
^{104}Ru	[15766 – 01 – 5]	18.7
osmium	[7440 – 04 – 2]	
^{184}Os	[14922 – 68 – 0]	0.02
^{186}Os	[13982 – 09 – 7]	1.58
^{187}Os	[15766 – 52 – 6]	1.6
^{188}Os	[14274 – 81 – 8]	13.3
^{189}Os	[15761 – 06 – 5]	16.1
^{190}Os	[14274 – 79 – 4]	26.4
^{192}Os	[15062 – 08 – 5]	41.0
rhodium-103	[7440 – 16 – 6]	100
palladium	[7440 – 05 – 3]	
^{102}Pd	[14833 – 50 – 2]	1.02
^{104}Pd	[15128 – 18 – 4]	11.14
^{105}Pd	[15749 – 57 – 2]	22.23
^{106}Pd	[14914 – 59 – 1]	27.33
^{108}Pd	[15749 – 58 – 3]	26.46
^{110}Pd	[15749 – 60 – 7]	11.72
iridium	[7439 – 88 – 5]	
^{191}Ir	[13967 – 66 – 3]	37.3
^{193}Ir	[13967 – 67 – 4]	62.7
platinum	[7440 – 06 – 4]	
^{190}Pt	[15735 – 68 – 9]	0.01
^{192}Pt	[14913 – 85 – 0]	0.79
^{194}Pt	[14998 – 96 – 0]	32.9
^{195}Pt	[14191 – 88 – 9]	33.8
^{196}Pt	[14867 – 61 – 9]	25.3
^{198}Pt	[15756 – 63 – 5]	7.2

1. Properties

The relative abundance of the stable isotopes of the PGMs and their CAS Registry Numbers are shown in Table 1.

1.1. Physical and Mechanical Properties

Whereas there are some similarities in the physical and chemical properties between corresponding members of the PGM triads, eg, platinum and palladium, the PGMs taken as a unit exhibit a wide range of properties (2). Some of the most important are summarized in Table 2.

The metals all have high melting points, ranging from 1552°C (Pd) to 3050°C (Os). Densities increase from 12.02 g/cm^3 (Pd) to 22.65 g/cm^3 (Ir), and electrical resistivity from 4.33 $\mu\Omega$·cm (Rh) to 9.93 $\mu\Omega$·cm (Pd) at 0°C. The crystal structures progress from the hexagonal close-packed (hcp) structures of ruthenium and osmium, which gives these metals properties similar to the refractory metals (hard, brittle, and relatively poor

Table 2. Properties of Platinum-Group Metals

Parameter	Ruthenium	Rhodium	Palladium	Osmium	Iridium	Platinum
atomic number	44	45	46	76	77	78
atomic weight	101.07	102.91	106.40	190.20	192.20	195.09
number of stable isotopes	7	1	6	7	2	6
elemental abundance, ppm	1×10^{-3}	1×10^{-3}	5×10^{-3}	1×10^{-3}	1×10^{-3}	1×10^{-2}
usual valency	3,4,6,8	3	2,4	4,6,8	3,4	2,4
ionic radius, pm	67	68	65	69	68	65
crystal structure[a]	hcp	fcc	fcc	hcp	fcc	fcc
lattice constant, a, pm	270.56	380.3	389	273.41	384	392.31
color	white	silvery	steel white	bluish	yellowish white	silvery
reflectance, %	63	79	54		64	55
melting point, °C	2310	1960	1552	3050	2443	1769
vapor pressure at mp, Pa[b]	1.31	0.133	3.47	1.8	0.467	0.0187
density, g/cm^3	12.45	12.41	12.02	22.61	22.65	21.45
heat capacity at 25°C, J/(°C·mol)[c]	24.06	24.98	25.98	24.70	24.50	25.85
thermal expansion, °C^{-1} × 10^6	9.1	8.3	11.11	6.10	6.8	9.1
magnetic susceptibility, cm^3/g	4.27×10^{-7}	9.9×10^{-7}	5.23×10^{-6}	5.2×10^{-8}	1.33×10^{-7}	9.71×10^{-7}
work function, eV		4.8	4.99			5.27
Young's modulus, kN/m^2	4.85×10^8	3.86×10^8	1.24×10^8	5.56×10^8	5.28×10^8	1.71×10^8
ultimate tensile strength, MPa[d]	500–600	400–560	180–200		400–500	120–160
Poisson's ratio	0.31	0.36	0.39	0.28	0.28	0.36
Vickers' hardness (VPN)	200–250	100–120	40	300–670	220	40
elongation, %	10	6.5	20–35			40
specific strength per unit cost, $\text{MPa}\cdot\text{cm}^3/(\text{g}\cdot\$)$[d]	6.66	0.17	0.26		0.72	0.06
temperature coefficient of resistance (TCR), K^{-1}	4.2×10^{-3}	4.6×10^{-3}	3.8×10^{-3}	4.2×10^{-3}	4.3×10^{-3}	3.9×10^{-3}
electrical resistivity at 0°C, $\mu\Omega\cdot$cm	6.8	4.33	9.93	8.12	4.71	9.85
thermal conductivity, W/(m·K)	119	153	75	88	147	73

[a] hcp = hexagonal close − packed; fcc = face − centered cubic·

[b] To convert Pa to mm Hg, multiply by 0.075.

[c] To convert J to cal, divide by 4.184.

[d] To convert MPa to psi, multiply by 145.

oxidation resistance) to the face centred cubic (fcc) structures of platinum and palladium, with properties akin to gold (soft, ductile, excellent resistance to oxidation and high-temperature corrosion). Vickers hardness of the annealed metals extends from 40–42 Vickers Pyramidal Number (VPN) (Pd and Pt) to 300–670 VPN (Os). Rhodium (up to 40%), iridium (up to 30%) and ruthenium (up to 10%) are often used to harden platinum and palladium, whose intrinsic hardness and tensile strength are too low for many intended applications. Many of the properties of rhodium and iridium are intermediate between these two extremes.

The mechanical and many other properties of the PGMs depend on their physical form, history and purity. For example, electrodeposited platinum is much harder than the wrought metal.

Ruthenium and osmium have hcp crystal structures. These metals have properties similar to the refractory metals, ie, they are hard, brittle, and have relatively poor oxidation resistance (see Refractories). Platinum and palladium have fcc structures and properties akin to gold, ie, they are soft, ductile, and have excellent resistance to oxidation and high temperature corrosion.

Hardness of the annealed metals covers a wide range. Rhodium (up to 40%), iridium (up to 30%), and ruthenium (up to 10%) are often used to harden platinum and palladium whose intrinsic hardness and tensile strength are too low for many intended applications. Many of the properties of rhodium and iridium, Group 9 metals, are intermediate between those of Group 8 and Group 10. The mechanical and many other properties of the PGMs depend on the physical form, history, and purity of a particular metal sample. For example, electrodeposited platinum is much harder than wrought metal.

1.2. Chemical Properties and Corrosion Resistance

Among the outstanding characteristics of the PGMs are exceptional resistance to corrosive attack by a wide range of liquid and gaseous substances, and stability at high temperatures under conditions where base and refractory metals are easily oxidized (3). This is owing to thermodynamic stability over a wide range of conditions and the formation of thin protective oxide films in aqueous media under oxidizing or anodic conditions. Electrochemical properties of the PGMs as these affect corrosion resistance are described in Reference 4. The PGMs are often used as sheaths, linings, electrodeposits, or other thin coatings on strong supporting structures. In many cases the strength, rigidity, hardness, and resistance to corrosion of the PGMs can be further improved by alloying, particularly with a second metal of the same group. Alloys of platinum with rhodium (up to 40 wt %), with iridium (up to 30 wt %), and with ruthenium (up to 10 wt %) are characterized by improved corrosion resistance and creep resistance as well as by greater hardness. However, alloys having higher alloying additions are more difficult to fabricate.

The PGMs are extremely resistant to corrosion by aqueous solutions of alkalies and salts and by dilute acids, and are generally quite resistant to more concentrated acids and halogens (Table 3) (5). In concentrated acids at high redox potentials, ie, under oxidizing conditions, there is a zone of corrosion. This accounts for the solubility of platinum in aqua regia. Rhodium is particularly resistant to chemical attack. In bulk form, rhodium is resistant even to aqua regia, although when finely divided this metal is attacked by concentrated sulfuric acid and aqua regia.

Of the nonmetals, phosphorus, arsenic, silicon, sulfur, selenium, tellurium, and carbon attack some or all of the metals at red heat, forming alloys or low melting point phases. Rhodium and iridium are resistant to fused lead oxide, silicates, molten copper, and iron at temperatures up to 1500°C. The PGMs are unaffected by most organic compounds, although the catalytic reactions that can occur on the surface of platinum and palladium result in an etched appearance of these metals. Palladium is much less resistant to chemical attack, especially by strong oxidizing acids at elevated temperatures (see Table 3). Palladium is stable in air, even at elevated temperatures, and shows no corrosion or tarnishing in hydrogen sulfide atmospheres. However, it has been reported that some discoloration owing to sulfide film formation may take place in industrial atmospheres containing sulfur dioxide (3).

1.3. High Temperature Properties

There are marked differences in the ability of PGMs to resist high temperature oxidation. Many technological applications, particularly in the form of platinum-based alloys, arise from the resistance of platinum, rhodium, and iridium to oxidation at high temperatures. Osmium and ruthenium are not used in oxidation-resistant applications owing to the formation of volatile oxides. High temperature oxidation behavior is summarized in Table 4.

Although platinum does not form a measurable oxide film, it is covered with a strongly held layer of adsorbed oxygen that volatilizes at an increasing rate above 1000°C, particularly in moving air or oxygen. Rhodium, iridium, and palladium exhibit oxide-film formation, as low as 600°C in the case of palladium.

Table 3. Corrosion Resistance of Platinum-Group Metals[a]

Medium	Ruthenium	Rhodium	Palladium	Osmium	Iridium	Platinum
chlorine at 20°C						
saturated	B	A	A		A	A
moist	A	A	D	C	A	B
dry	A	A	C	A	A	B
bromine at 20°C						
saturated	B	A	B		A	A
moist	A	A	D	B	A	C
dry	A	A	D	D	A	C
iodine at 20°C						
in alcohol	B	B	B		A	A
moist	A	B	B	A	A	A
dry	A	A	A	B	A	A
HBr, 62% conc						
7 h, 100°C	A	B	C		A	B
25°C	A	B	D	A	A	B
HCl, 36% conc, 7 h, 25°C	A	A	A	A	A	A
HI, 60% conc, 4 h, 25°C	A	A	D	B	A	A
HF, 40% conc, 25°C	A	A	A	A	A	A
aqua regia, 25°C	A	A	D	D	A	D
H_2SO_4, 98% conc, 7 h						
25°C	A	A	A	A	A	A
300°C	A	D	C		A	B
H_3PO_4, 10% conc, 5 h, 100°C	A	A	B		A	A
HNO_3, 95% conc, 25°C	A	A	D	D	A	A
selenic acid, 95% conc, 25°C			C			A
fused NaOH, 1 h, 330°C	C	B	B		B	
fused NaCN, 1 h, 700°C	D	D	D		C	D

[a] A = no appreciable corrosion; B = some attack, but not enough to preclude use; C = attacked enough to preclude use; and D = rapid attack.

Table 4. High Temperature Oxidation Behavior

Metal	Behavior
ruthenium	readily oxidizes to RuO_2 if heated in air or oxygen
rhodium	tarnish-resistant at room temperature; superficial oxidation when heated in air to red heat, but oxide decomposes above 1100°C; visible as dark discoloration
palladium	not tarnished by dry or moist air at room temperature, but at about 600°C a thin oxide film forms in air; above 800°C the superficial oxide decomposes, leaving a clean metal surface; some dissolution or oxide formation occurs again above 1000°C
osmium	volatile oxide OsO_4 is formed by action of cold air on the finely divided metal, although the compact metal must be heated before oxidation occurs
iridium	superficial oxidation when heated in air, but oxide dissociates above 1140°C
platinum	no oxide film forms; retains metallic luster on heating in air up to its melting point, even in sulfur-bearing industrial atmospheres; volatilizes above 1000°C

Palladium oxide dissociates again above 800°C, the metal appearing bright up to its melting point. However, absorption of oxygen without film formation occurs and the palladium increases in weight. Rhodium and iridium are less volatile than platinum in the temperature range of 900–1200°C, but are about equal at 1300°C.

No single metal in the platinum group possesses all the desirable characteristics necessary for industrial high temperature applications. However, most high temperature applications for platinum utilize its freedom from corrosion and oxidation, and alloying additions are thus chosen to preserve this characteristic (6). Improved high temperature strength is obtained by alloying with rhodium or iridium. Rhodium–platinum alloys show no preferential loss of either metal at high temperature and are widely used. Iridium–platinum alloys show greater loss of weight on heating in air, because of the greater rate of oxidation of iridium and the higher volatility of the oxide of this metal. Iridium is thus lost preferentially from this alloy. Below 1100°C, alloys of platinum with rhodium or palladium are less volatile than pure platinum. However, the oxygen-absorbing properties of palladium prevent its application in alloy form at high temperatures.

Pure platinum and its alloys are subject to grain growth when operated for long periods at high temperature, resulting in mechanical failure owing to weaknesses from large intercrystal boundaries. This problem is alleviated by the incorporation of a small amount of refractory oxide, such as zirconia, to form a range of grain-stabilized materials. Zirconia grain-stabilized (ZGS) platinum and ZGS 10% rhodium–platinum are considerably stronger and have longer life at high temperatures than the corresponding pure metal or alloy.

1.4. Catalytic Properties

All the PGMs, but particularly platinum and palladium, show catalytic properties for a variety of chemical reactions, including hydrogenation, oxidation, isomerization, and carbon–carbon bond formation.

A fundamental measure of catalytic activity is heat of adsorption, which is a measure of how strongly a reactant bonds to a surface. If the reactant is too strongly adsorbed, it will be bonded too strongly to the surface to react with other bonded species. Weakly bonded substances require only a small amount of energy to displace them from the surface and are desorbed so quickly that they do not have time to react. The surface is effectively noncatalytic for these reactants. Effective catalysts operate between these two extremes. Platinum is unique in that a wide spectrum of substances are adsorbed with moderate strength, making it catalytically active for a wide range of reactions. These substances include hydrogen, oxygen, carbon monoxide, unsaturated hydrocarbons, nitrogen compounds (imines, azines, hydrazones, oximes), oxygenated compounds (acids, esters, anhydrides, aldehydes, ketones), sulfur dioxide and ammonia. Methane is only weakly adsorbed, and platinum must be doped with other metals to improve its ability to act as a methane combustion catalyst.

The catalytic properties of the PGMs are the basis of many major applications, for example automotive catalysts and in the chemical and petrochemical industries (see Uses section).

2. Sources and Production

Total known world resources of platinum-group metals have been variously estimated as between 68,000 (7) and 96,000 metric tons (8). Assuming the former estimate and 1979 levels of demand, these reserves should be sufficient to supply the Western world well into the twenty-fourth century. Reserves and relative proportions of the PGMs in the larger deposits are given in Tables 5 and 6. Relative amounts of the PGMs vary from deposit to deposit.

Almost all known deposits of platiniferous ores are related to basic igneous rocks. In many of the deposits, including those in South Africa, Canada, and the CIS, the PGM-containing ores occur in association with nickel, copper (qv), and iron sulfides. There are over 90 known minerals of the PGMs (9), of which the most numerous are the minerals of palladium, followed by platinum. However, there are few native minerals of iridium, osmium, and ruthenium. Rhodium is only known to exist as two minerals: native rhodium and hollingworthite. Rhodium is usually found as impurities dispersed throughout the other PGM minerals. The PGM minerals can be divided into three classes: (*1*) native platinoids and their native alloys; (*2*) intermetallic compounds between PGMs and other metals and semimetals such as Sn, Pb, Bi, Sb, and Te; and (*3*) sulfides, arsenides, and sulfoarsenides of the platinoids. The most common PGM-containing minerals occurring in significant deposits are listed in Table 7.

Table 5. Estimated Reserves of PGMs and Gold, t[a]

	Bushveld Igneous Complex, South Africa			Sudbury, Canada	Noril'sk, CIS	Stillwater, Montana
PGM	Merensky Reef	UG2	Platreef			
platinum	10,360	13,590	4,980	105	1,550	220
palladium	4,380	11,350	5,440	110	4,420	715
ruthenium	1,400	3,890	470	<30	60	45
rhodium	530	2,580	375	<30	190	85
iridium	190	750	95	<30		<30
osmium	150		60	<30		
gold	560	220	400	<35		<30
Total	*17,570*	*32,380*	*11,820*	*280*	*6,220*	*1,090*
grade, g/t	8.1	8.7	7–27	0.9	3.8	22.3

[a] Ref. 7.

Table 6. Relative Proportions of the PGMs in Deposits, %[a]

	Bushveld Igneous Complex, South Africa			Sudbury, Canada	Noril'sk, CIS	Stillwater, Montana
PGM	Merensky Reef	UG2	Platreef			
platinum	59	42	42	38	25	19
palladium	25	35	46	40	71	66.5
ruthenium	8	12	4	2.9	1	4
rhodium	3	8	3	3.3	3	7.6
iridium	1	2.3	0.8	1.2		2.4
osmium	0.8		0.6	1.2		
gold	3.2	0.7	3.4	13.5		0.5

[a] Ref. 7.

Table 7. Most Common Minerals in Primary PGM Deposits[a]

Deposit	Mineral	Composition
Merensky Reef	ferroplatinum	$\mathrm{Pt_3Fe}$
	braggite	$\mathrm{(Pt,Pd,Ni)S}$
	cooperite	PtS
	moncheite	$\mathrm{PtTe_2}$
	sperrylite	$\mathrm{PtAs_2}$
Sudbury	sperrylite	$\mathrm{PtAs_2}$
	moncheite	$\mathrm{PtTe_2}$
	michenerite	PdBiTe
Noril'sk	ferroplatinum	$\mathrm{Pt_3Fe}$
	atokite	$\mathrm{Pd_3Sn}$
	rustenburgite	$\mathrm{Pt_3Sn}$
	zvyagintsevite	$\mathrm{Pd_3Pb}$
	paolovite	$\mathrm{Pd_2Sn}$
	plumbopalladinite	$\mathrm{Pd_3Pb_2}$
	polarite	$\mathrm{Pd(Pd,Bi)}$–$\mathrm{Pd(Bi,Pb)}$
	sperrylite	$\mathrm{PtAs_2}$
	kotulskite	PdTe
	cooperite	PtS
	vysotskite	$\mathrm{(Pd,Ni,Pt)S}$

[a] Ref. 9.

In South Africa, PGM deposits are found within a geological area known as the Bushveld Igneous Complex, an area covering approximately 650,000 km^2 in the Central Transvaal. Commercially, the most important deposit within the Bushveld Complex is the Merensky Reef, whose PGM reserves have been estimated (7) as 17,600 metric tons with an average grade of 8.1 g/t. Deposits of platinum itself are thought to be 10,400 metric tons. The Merensky Reef has an average thickness of only 500 mm, but is generally continuous, with relatively little faulting. Exploitation is facilitated by the relatively shallow depth of the Merensky Reef, which in places outcrops at the surface.

There are two other known deposits of PGM in the Bushveld Complex. The UG2 deposit has a thickness of approximately 600 mm, and is located between 36 and 330 meters below or parallel to the Merensky Reef, allowing it to be mined from the same access shafts. UG2 is of a higher grade than the Merensky Reef (8.7 g/ton PGM vs 8.1 g/ton) and contains nearly three times as much rhodium as the Merensky Reef. Until recently, UG2 has not been exploited commercially, as its high chromite content made smelting difficult. However, refining methods have now been developed that allow the chromium to be exploited as ferrochromium. Commercial production from UG2 began in the mid-1980s.

The Platreef deposit is located at the contact between the Bushveld Complex and the underlying rocks. It is disseminated and erratic, with a pgm grade between 7 and 27 g/t. Its proximity to the surface allows open cast mining, and the high nickel content provides valuable additional revenue. Although Platreef was mined briefly in the 1920s, research into its exploitation has increased dramatically in recent years. Commercial mining began here in 1993.

The majority of Russian PGM is a by-product of nickel and copper mining at Noril'sk-Talnakh in Northern Siberia. Russian PGM-containing ores fall into two distinct types. Massive sulfides have an average pgm content between 5 and 15 g/ton, with localized deposits containing as much as 60 g/ton. Disseminated ores contain about 5 g/t PGM. Noril'sk ores are particularly rich in palladium, which accounts for over 70% of the pgm content of the ore.

In Canada, PGMs are present in the extensive nickel and copper sulfide deposits around Sudbury, Ontario. PGM ores containing between 13 and 22 g/t occur at Stillwater, Montana in the United States.

Extensive PGM deposits exist on the Great Dyke in Zimbabwe. These are geologically similar to the Bushveld Complex in South Africa and it has been estimated they could produce up to 4.7 tons of platinum, 3.4 tons of palladium and 0.35 tons of rhodium annually. Limited commercial exploitation is now underway (see section on Economic Aspects). There are believed to be extensive PGM deposits in China, occuring in conjunction with nickel deposits around Jinchang in the north center of the republic. There has been an increased amount of speculative exploration of the widespread PGM deposits in Western Australia, but exploitation is not currently regarded as viable.

3. Recovery and Refining Techniques

In order to separate the PGMs from each other and from other metals at high yield, high percentage recovery, and high purity, a multistage refining process has been developed. The actual series of processing steps that the ore undergoes varies according to the composition and grade of that ore, and the source from which it was obtained. Raw material from the Merensky Reef requires a completely different pretreatment process to PGM-containing anode slimes, produced as a by-product of nickel electrorefining. The refining processes are tailored to each particular material. Every refinery has developed its own specific reagents and separation technology. The processes described herein are intended to give an indication of the stages required, and the physical and chemical principles controlling each separation. The procedures used by any particular refinery may differ in detail from those described.

3.1. PGM Concentration

The ore mined from the Merensky Reef in South Africa has a maximum PGM content of 5–8 g/t, of which 50–60% is platinum, and 20–25% palladium. The PGMs are in the form of a ferroplatinum alloy, or as their sulfides, arsenides, or tellurides. The aim of the concentration process is to separate from the ore a crude metal concentrate, having a PGM content of 60%. The majority of other metals, such as nickel and copper, are separated out at this stage for further refining.

A typical concentration process used for the ore of Merensky Reef origin is depicted in Figure 1. The crude ore is crushed and pulverized, using a series of jaw crushers followed by primary and secondary ball mills. The metal sulfide particles are then separated from the gangue by froth flotation using the following steps: air is introduced into a suspension of finely divided ore in water containing a frothing agent to produce a foam and further reagents to promote hydrophobicity on the PGM and base metal minerals. These then adhere to the surface of the air bubbles and rise to the surface where they can be separated from those minerals that are hydrophilic and remain in the liquid pulp. The flotation concentrate now has a PGM content of about 100–150 g/t. Conventional gravity concentration is used to separate out free, large, and dense PGM particles (typically 30–40% of the PGM), which can go straight to the refining process. The PGM sulfide pulp is prepared for smelting by thickening, filtering, and drying. It is smelted in an electric furnace, in the presence of fluxes and other additions, to produce a matte containing principally copper, nickel, iron sulfides, and PGMs. The sulfur content of the matte is reduced by converting with oxygen, and the matte is slow-cooled (see Mineral recovery and processing).

The resultant matte contains copper, nickel, cobalt, and PGMs, including 700–1000 g/t platinum. Nickel and copper are separated magnetically, refined, and marketed (see Separation, magnetic). The nonmagnetic component is pressure-leached to yield the final concentrate, which has a PGM content of approximately 60%. The gravity concentrate separated out earlier and the magnetic concentrate are then refined, using either a conventional or a solvent extraction process.

3.2. Conventional Refining Process

The conventional refining process is based on complex selective dissolution and precipitation techniques. The exact process at each refinery differs in detail (10–12), but a typical scheme is outlined in Figure 2.

The PGM concentrate is attacked with aqua regia to dissolve gold, platinum, and palladium. The more insoluble metals, iridium, rhodium, ruthenium, and osmium remain as a residue. Gold is recovered from the aqua regia solution either by reduction to the metallic form with ferrous salts or by solvent-extraction methods. The solution is then treated with ammonium chloride to produce a precipitate of ammonium hexachloroplatinate(IV), $(NH_4)_2PtCl_6$. Calcination of the precipitate gives Pt sponge, which can undergo further purification. The remaining aqua regia solution is treated with ammonium hydroxide, followed by hydrochloric acid, to precipitate dichlorodiammine-palladium. Calcination of this gives impure palladium sponge.

The Ir, Ru, Rh, and Os-containing residue from the original aqua regia dissolution is fused with lead carbonate and carbon. After solidification of the melt, the slag is removed, leaving a lead phase containing the PGMs and silver. This lead phase is melted, granulated, and treated with hot nitric acid to dissolve and separate lead and silver for recovery. The insoluble residue contains the minor PGMs. The residue is fused with sodium bisulfate; rhodium forms soluble rhodium sulfate, which can be leached out with water. A multistage dissolution and recrystallization process is then used to produce pure rhodium.

The residue, which contains Ir, Ru, and Os, is fused with sodium peroxide at 500°C, forming soluble sodium ruthenate and sodium osmate. Reaction of these salts with chlorine produces volatile tetroxides, which are separated from the reaction medium by distillation and absorbed into hydrochloric acid. The osmium can then be separated from the ruthenium by boiling the chloride solution with nitric acid. Osmium forms volatile

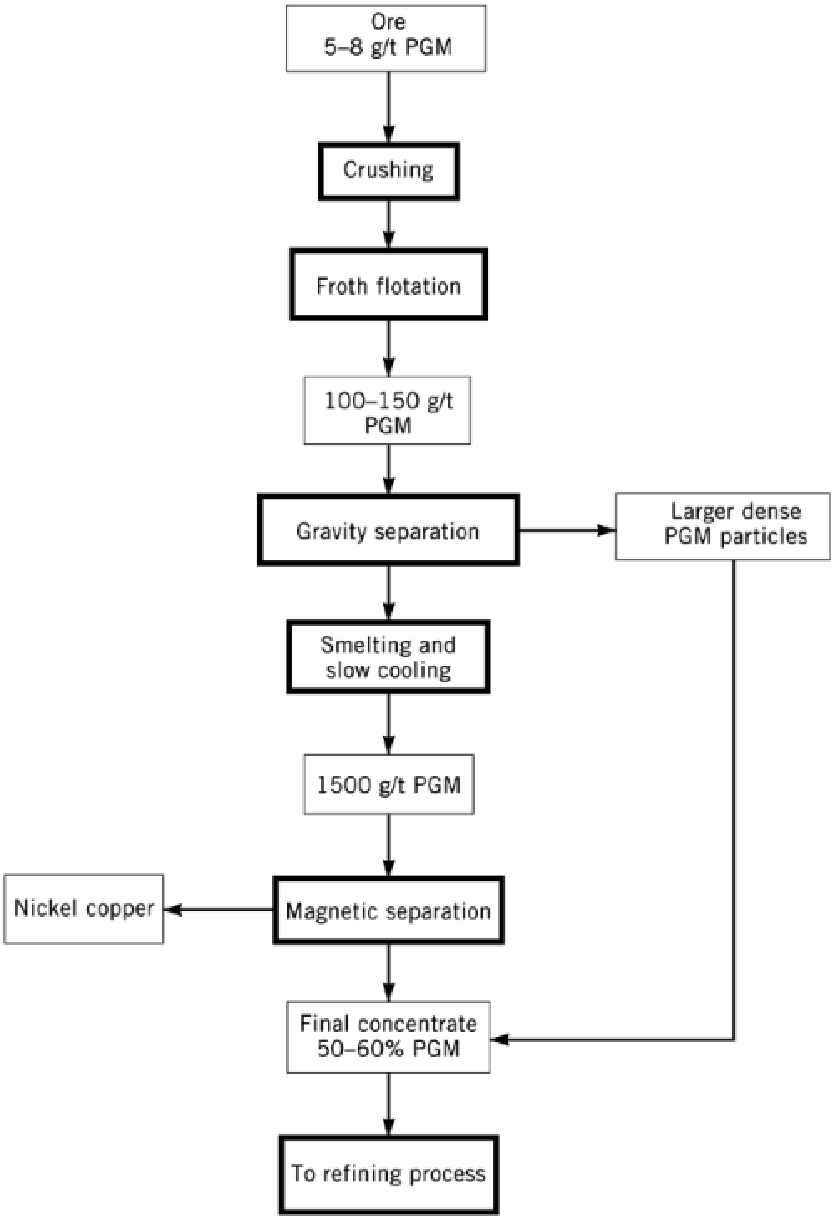

Fig. 1. Concentration process for ore of Merensky Reef origin, where (⧈) indicate stages of the process and (□), the product obtained.

osmium tetroxide; ruthenium remains in solution. Ruthenium and osmium can thus be separately purified and reduced to give the metals.

Insoluble iridium dioxide from the sodium peroxide fusion is dissolved in aqua regia, oxidized with nitric acid, and precipitated with ammonium chloride as impure ammonium hexachloroiridate(IV), $(NH_4)_2IrCl_6$. To purify this salt, it is necessary to redissolve the compound and precipitate out the impurities as sulfides. Nitric

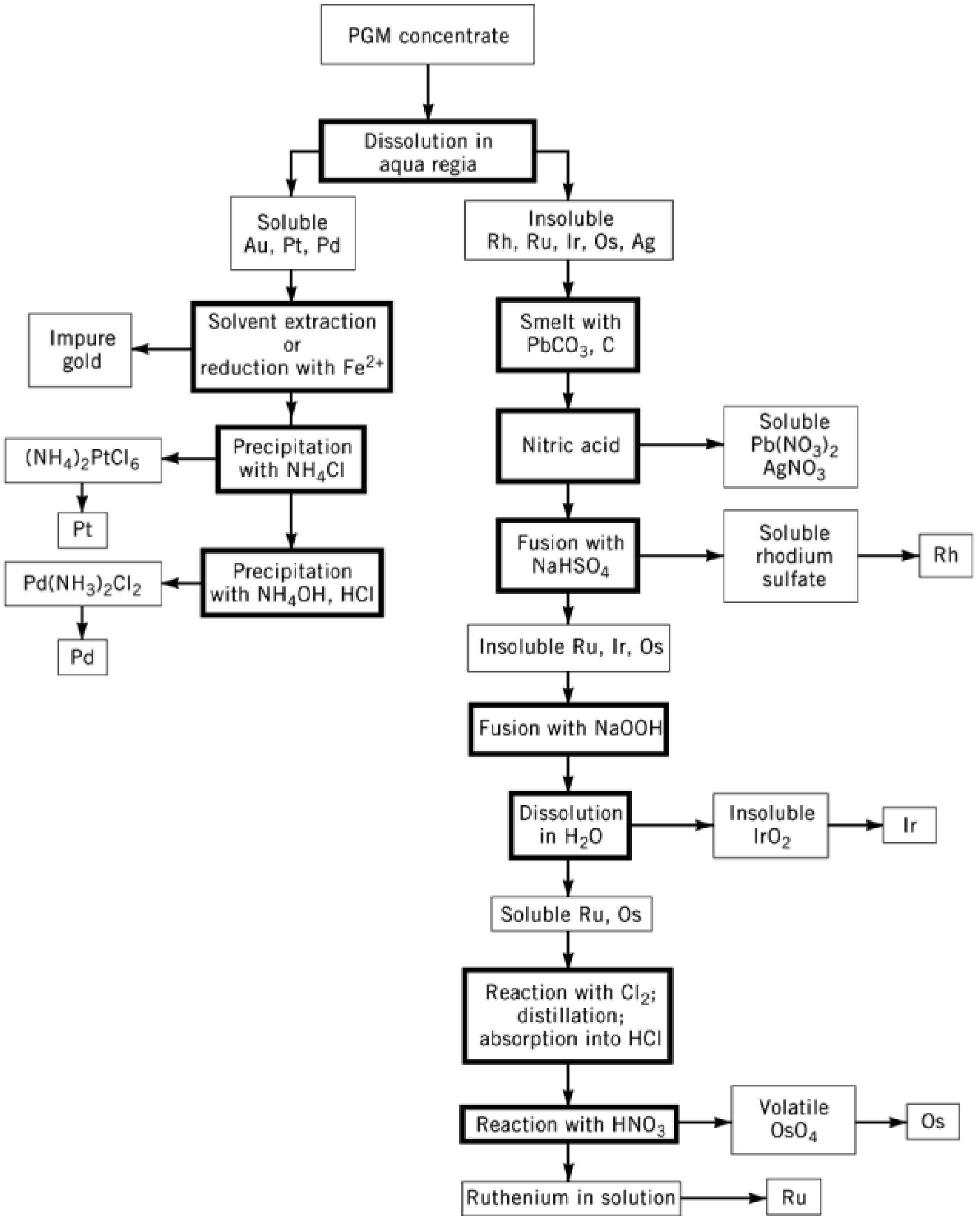

Fig. 2. Conventional PGM refining process. See Figure 1 for definitions.

acid and ammonium chloride are again used to produce pure ammonium chloroiridate, which is ignited and reduced with hydrogen to give iridium metal.

The disadvantage of the conventional refining process is that any single dissolution–reprecipitation step does not give a complete separation of the metals. The separation efficiency is hence low. Coprecipitation occurs, and the structure of the precipitate means that filtrate often becomes trapped. There is a need for repeated washing and filtration cycles, resulting in a long, labor-intensive process. Precious metals are thus tied up for long periods of time. The many filtrates and residues also require recovery or retreatment.

3.3. Solvent Extraction Technology

The use of solvent extraction technology to replace traditional processes has been the subject of considerable research and development effort since the 1970s (10, 12–19). This newer technique was being used commercially as of 1995 in at least three of the principal refineries.

The principle of solvent extraction in refining is as follows: when a dilute aqueous metal solution is contacted with a suitable extractant, often an amine or oxime, dissolved in a water-immiscible organic solvent, the metal ion is complexed by the extractant and becomes preferentially soluble in the organic phase. The organic and aqueous phases are then separated. By adding another aqueous component, the metal ions can be stripped back into the aqueous phase and hence recovered. Upon the identification of suitable extractants, and using a multistage process, solvent extraction can be used to extract individual metals from a mixture.

Solvent extraction is a relatively high cost process, owing to the specialty organic extractants required and the expenses of recovery and storage of organic solvents. However, in a precious-metal recovery operation, these costs are easily outweighed by the increased efficiency and PGM recovery as well as shortened metal-in-process time.

All solvent extraction processes are based on the chloro complexes of the PGMs, as chloride is the only effective medium by which the PGMs can be brought into solution. Selection of suitable extractants utilizes aspects of the aqueous chemistry of the metal species, such as the nature of the complex ionic species and the various redox potentials. In general, the PGMs form more stable complexes than the base metals. The most stable PGM complexes are those having heavier donor atoms. As an approximation, the overall order of stability is $\mathrm{S} \sim \mathrm{C} > \mathrm{I} > \mathrm{Br} > \mathrm{Cl} > \mathrm{N} > \mathrm{O} > \mathrm{F}$. Use of extractants forming particularly stable complexes, eg, by using sulfur ligands such as thioethers, allows good partition into the organic phase. However, the strength of the complex formed makes stripping of the metal back into the aqueous phase difficult.

The actual solvent extraction processes used, including the specific extractants and the order in which the components are separated, vary from refinery to refinery. However, a typical scheme is shown in Figure 3 (12).

The raw precious metal concentrate is totally dissolved in hydrochloric acid–chlorine solution to form the soluble chloride ions of each of the metals. Silver remains as insoluble silver chloride and can be filtered off. Gold, in the form of $[\mathrm{AuCl_4}]$, is extracted with, eg, tributyl phosphite or methyl isobutyl ketone. Base metals are also extracted in this step, and are removed from the organic phase by scrubbing with dilute hydrochloric acid (HCl). Iron powder is then used to reduce the gold species and recover them from the organic phase.

Palladium is extracted using a beta-hydroxyoxime, which undergoes a ligand exchange reaction with $[\mathrm{PdCl_4}]^{2-}$. The resulting organic phase is again scrubbed with dilute HCl to separate base metals. The palladium is stripped from the organic phase into aqueous ammonium hydroxide solution, and finally precipitated with hydrochloric acid. The remaining solution is neutralized, allowing the osmium and ruthenium to be separated as their volatile tetroxides. Distillation can later be used to separate these two metals. After reduction of the solution using sulfur dioxide to convert Ir(IV) to Ir(III), $[\mathrm{PtCl_6}]^{2-}$ is extracted using a tertiary amine, tri-*n*-octylamine. Hydrochloric acid is used to strip the platinum from the organic phase, and ammonium chloride is used to precipitate it as $\mathrm{(NH_4)_2PtCl_6}$.

Subsequently, the PGM solution is oxidized and acidified to reconvert Ir(III) to Ir(IV). Tri-*n*-octylamine is again used as the extractant, this time to extract iridium. The iridium in the organic phase is reduced to Ir(III) and recovered. The remaining element is rhodium, which is recovered from impurities in the original solution by conventional precipitation or ion exchange (qv).

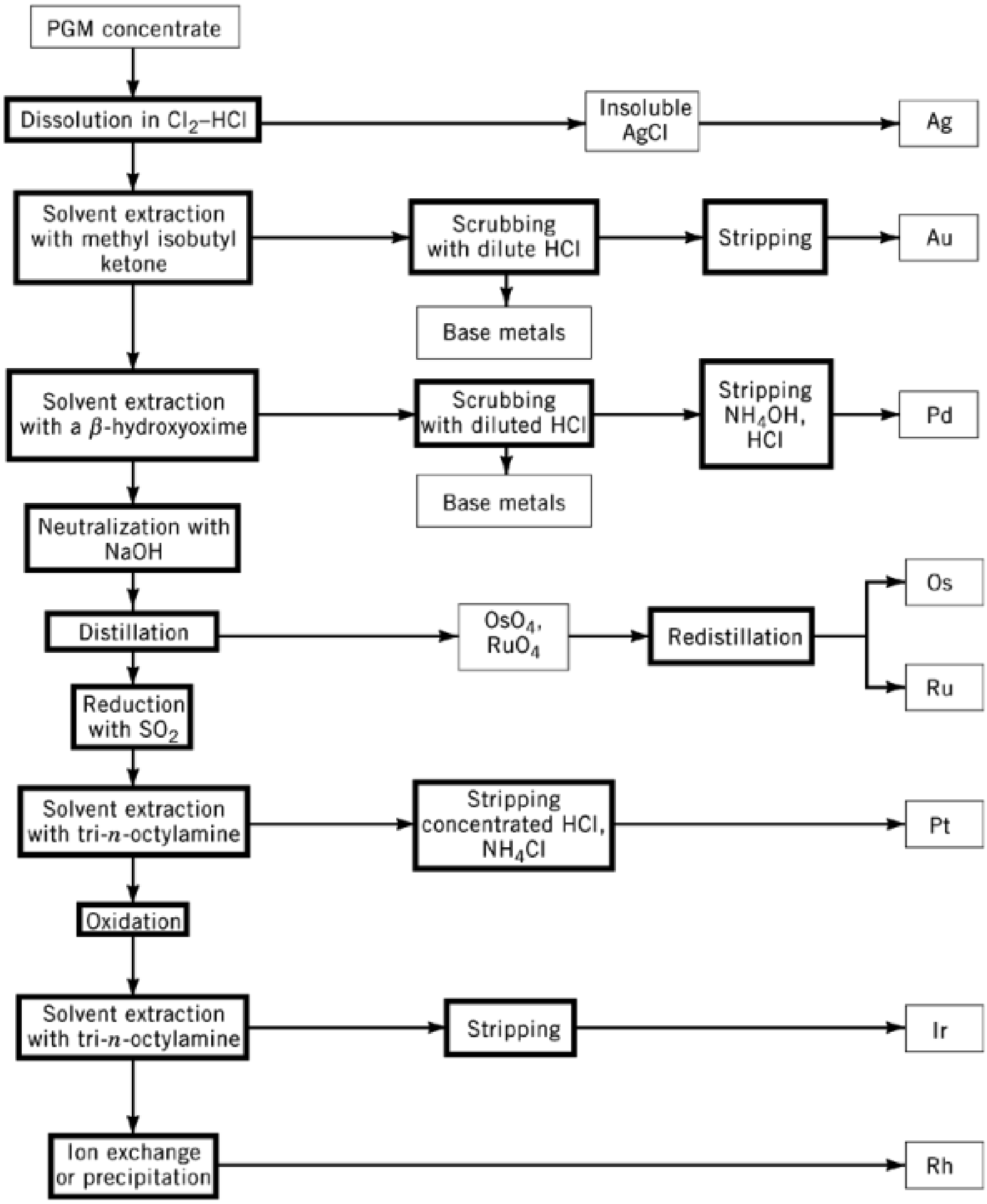

Fig. 3. PGM refining by solvent extraction. See Figure 1 for definitions.

3.4. Secondary Platinum-Group Metals

For many PGM applications, the actual loss during use of the metal is small, and hence the ability to recover the PGM efficiently contributes greatly to the economics of PGM use. Typical sources of PGM for secondary refining include jewelry and electronics scrap, catalysts, and used equipment, eg, from the glass industry.

In recent years, spent automotive catalysts have emerged as a source of secondary Pt, Pd, and Rh with major potential. However, supplies of PGM from autocatalyst recovery have grown more slowly than many in the platinum industry expected. Between 1975 and 1995, more than 600 t of platinum have been used in autocatalysts, but by the end of 1995 only about 60 t had been recovered. Much of the remaining 540 t is still installed in vehicles, but some has been irretrievably lost, principally because the catalysts on scrapped vehicles are not always removed and processed.

The collection and processing of spent catalysts occurs along similar lines in all areas of the world. When a car reaches the end of its useful life, it is sent for dismantling at a scrap yard, where the valuable parts, including the catalytic converter, are removed before the vehicle is shredded. The scrap dealer sells the converters to a collector, who in turn sells them on to a specialist processor. The first step in recovering PGM is to remove the ceramic substrate coated with the catalytic metals from its stainless steel container. This is performed by placing the converter in a machine with a heavy blade, which drops down and splits open the can. In most cases the ceramic material is then smelted (20, 21). The smelting process yields a PGM-containing concentrate, from which pure metals are recovered in a specialist PGM refinery.

Other processes which are used for the recovery of PGM from spent automotive or petroleum industry catalysts include: (*1*) Selective dissolution of the PGM from the ceramic support in aqua regia. Soluble chloro complexes of Pt, Pd and Rh are formed, and reduction of these gives crude pgm for further refining, (*2*) Dissolution of the catalyst support in sulfuric acid, in which platinum is insoluble. This technique is widely used for the treatment of γ-alumina petroleum catalysts, but is not suitable for the dissolution of cordierite honeycomb substrates (often used in automotive catalysts) (*3*). A gas-phase volatilisation process has also been reported (22). The PGMs are selectively chlorinated to give volatile compounds, and condensed in a cooler zone. In principle, the ceramic substrate does not react.

Recovery from the smelting and refining processes are relatively high. About 95% of the platinum and palladium and about 80% of the rhodium remaining in the spent catalyst can be reclaimed. However, some metal may be lost elsewhere. The ceramic substrate may be damaged during the decanning process and this leads to losses of PGM-containing material. Poor engine maintenance can also sometimes result in the degradation of the catalytic converter in use, although this problem is becoming less significant with the development of advanced engine management systems and the introduction of more durable autocatalysts.

The United States is the most important source of PGM from spent catalytic converters and a well-organized network for their collection and processing is in place. This leading position is largely because of the country's long experience with catalyst fitment. Even so, not all scrapped catalysts find their way into the reprocessing network. For example, some vehicles are shredded with the catalyst still in place. These numbers are declining because most scrap dealers are now alert to the value of PGM-containing material. Some cars never make it to the scrap yard, either being abandoned or exported to countries in Latin America where catalyst collection is virtually nonexistent.

Strict emission controls did not come into force in Europe until 1993 so only a relatively small proportion of the cars currently being scrapped are fitted with catalysts. Consequently the collection and processing networks are generally in the early stages of development. As more autocatalyst scrap becomes available, steady growth in European recovery is expected.

4. Economic Aspects

4.1. Suppliers

Production of PGMs is dominated by South Africa and Russia, with lesser amounts produced in Canada and the United States.

4.1.1. South Africa

South Africa is by far the largest producer of primary (newly mined) PGMs. In 1998, it supplied almost 70% of the platinum used in the West, and over 50% of all the PGMs. In South Africa, PGMs are mined as the primary product, with other metals such as nickel, copper, and cobalt as by-products. The majority of South African PGM mines are operating close to capacity, and each of the operators is looking at ways of increasing production. These include the commissioning of new mines and the expansion of existing mines, and capital projects to give improvements in grades and recoveries from processing and refining operations.

PGM mining in South Africa is controlled by three main companies, Amplats, Impala, and Lonmin (formerly Lonrho). Amplats (which includes the Rustenberg Platinum, Lebowa Platinum and Potgietersrust Platinum (PPRust) mines) is the largest of the four companies, and is responsible for about 50% of refined platinum production. Impala Platinum is responsible for about 28% of South African refined platinum production. It mines PGM from both the Merensky Reef and UG2 deposits, and has recently commissioned new declines and shafts in the Merensky Reef, to reduce dependence on lower grade UG2 ores. Lonmin accounts for about 17% of refined platinum production.

A fourth producer, Northam Platinum, began producing platinum in 1992 and today accounts for about 5% of refined platinum production. Mining is expected to start during 1999, by a new mining company, Kroondal Platinum.

4.1.2. Russia

This is the second most important PGM-producing country overall, but is particularly significant for palladium, supplying over 60% of global palladium demand. The majority of Russian PGM is produced as a by-product of nickel and copper mining at Noril'sk-Talnakh in Northern Siberia.

The total production capacity of the Noril'sk mines is about 14×10^6 metric tons of ore per year. This corresponds to between 60 and 200 tons PGM. However, it is thought that sales of Russian PGM are significantly higher than actual production, and that large amounts of metal are supplied from Government stockpiles. Current stockpiles of platinum and rhodium are thought to be low, although there are probably still large reserves of palladium.

Russian supplies of PGM tend to be erratic and there have been several major disruptions to PGM export in the last few years. Historically, export of PGM has been under strict central Governmental control, with sales being made by the marketing agency Almaz. At the end of 1996, the Russian Committee for Precious Metals and Stones (Roskomdragmet) was dismantled and its duties divided between the Ministry and Finance and the Ministry of Industry. During this reorganization, no one had clear responsibility for export quotas and licences. Hence no PGM was exported from Russia between January and July 1997, and again for several months during 1998, while budgets and PGM quotas were finalized by the Government.

More recently, Noril'sk Nickel has been awarded a long-term export quota, using Almaz as its agent. This allows it to export palladium over a ten-year period and should enable it to enter long-term supply agreements with western consumers.

4.1.3. North America

North American mines produced about 8.9 metric tons of platinum and 20.5 metric tons of palladium in 1998. In Canada, the two main producers of PGMs are Inco and Falconbridge, both of whom produce pgms as a byproduct of nickel mining. A third Canadian producer, North American Palladium produced about 2.5 metric tons of palladium in 1998 (23). Stillwater operates a platinum and palladium mine in Montana, U.S., and produced about 14 tons of platinum and palladium in 1998.

Table 8. World Platinum Supply, t[a]

Regions	*1987*	*1990*	*1993*	*1996*	*1997*	*1998*
South Africa	78.4	85.8	104.5	105.4	115.1	114.4
North America	4.4	5.8	6.5	7.5	7.5	8.9
Russia	12.4	22.4	21.2	37.9	28.0	40.4
other	1.2	2.0	4.0	4.0	4.0	4.2
Total	*96.4*	*116.0*	*136.2*	*154.9*	*154.6*	*167.9*

[a] Ref. 24.

Table 9. Platinum Demand by Region, t[a]

Region	*1987*	*1990*	*1993*	*1996*	*1997*	*1998*
Western Europe	17.40	21.80	27.80	26.1	27.1	27.8
Japan	51.30	57.50	61.00	62.4	58.6	56.1
North America	28.00	24.60	23.80	36.7	40.3	40.9
rest of world	5.60	11.20	13.10	29.1	34.8	41.5
Total[b]	*102.3*	*115.1*	*125.6*	*154.3*	*160.8*	*166.3*

[a] Ref. 24.

[b] Demand figures do not include 1.2 metric tons sold to China in 1987 and 0.6 tons to China in 1993. Chinese data for later years is incorporated in the Rest of World region.

Table 10. Platinum Demand by Application, t

Industry	*1987*	*1990*	*1993*	*1996*	*1997*	*1998*
autocatalyst	39.0	47.7	52.9	58.5	58.2	56.9
gross recovery	3.6	6.7	8.9	10.9	11.5	12.6
chemical	6.10	6.70	5.70	7.2	7.3	8.2
electrical	5.60	6.40	5.40	8.6	9.5	10.0
glass	3.70	4.20	2.20	7.9	8.2	6.8
investment	15.20	6.20	9.50	7.5	7.5	9.8
jewelery	30.80	42.40	50.10	61.9	67.2	73.7
petroleum	1.70	4.40	3.10	5.8	5.3	4.0
other	3.70	3.70	5.60	7.9	9.2	9.5
Total	*102.3*	*115.1*	*125.6*	*154.30*	*160.80*	*166.3*

4.1.4. Other

Since 1997, small amounts of refined PGM have been mined and sold by Hartley Platinum in Zimbabwe. This mine has yet to reach full capacity. Other companies such as Anglo American Zimbabwe and Zimbabwe Platinum Mines Ltd (Zimplats) are planning other platinum projects in Zimbabwe.

4.2. Supply and Demand

Tables 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18 show global supply and demand statistics for platinum, palladium, and ruthenium. These figures are derived from the *Platinum* series. In the Tables, the demand figures are net figures, representing total purchases of the metals by customers, minus any sales back to the market. However, for autocatalyst applications, figures for both gross PGM demand and recycled metal are given.

Figure 4 shows the average prices for platinum, palladium, and rhodium from 1995–1998. In December 1998, platinum averaged $11.30/g, palladium $9.80/g, rhodium $23.20, iridium $13.30/g and ruthenium $1.30/g.

Table 11. Palladium Supply, t[a]

Region	*1987*	*1990*	*1993*	*1996*	*1997*	*1998*
South Africa	33.9	38.2	43.4	52.6	56.3	56.6
North America	5.9	11.5	11.5	14.2	16.9	20.5
others	2.8	2.2	2.2	3.0	3.0	3.7
Russia[b]	42.6	58.2	71.5	174.2	149.3	180.4
Total	*97.4*	*110.1*	*128.6*	*244.0*	*225.5*	*261.2*

[a] Ref. 24.
[b] Sales.

Table 12. Palladium Demand by Region, t[a]

Region	*1987*	*1990*	*1993*	*1996*	*1997*	*1998*
Western Europe	17.1	18.3	21.1	47.4	56.3	63.1
Japan	44.5	47.6	61.9	58.6	73.2	64.8
North America	32.2	33.6	40.3	68.0	80.1	105.5
rest of world	5.3	6.7	9.3	17.3	22.4	21.3
Total demand	*99.1*	*106.2*	*132.6*	*191.3*	*232.0*	*254.7*

[a] Ref. 24.

Table 13. Palladium Demand by Application, t[a]

Industry	*1987*	*1990*	*1993*	*1996*	*1997*	*1998*
autocatalyst	8.4	9.8	21.9	73.4	96.4	139.0
gross recovery	1.6	2.6	3.1	4.5	4.5	5.4
chemical	5.3	6.7	5.9	7.5	7.5	7.1
dental	29.7	31.7	37.6	41.1	42.0	38.2
Electrical	49.0	52.1	62.7	62.8	78.1	64.4
Jewelery	5.1	6.1	6.5	6.7	8.1	7.8
other	3.1	2.5	1.1	4.4	4.5	3.6
Total	*99.1*	*106.2*	*132.6*	*191.3*	*232.0*	*254.7*

[a] Ref. 24.

Table 14. Rhodium Supply, t[a]

Region	*1987*	*1990*	*1993*	*1996*	*1997*	*1998*
South Africa	6.1	6.2	8.6	11.2	11.7	12.5
North America	0.6	0.5	0.5	0.2	0.4	0.5
other	0.00	0.00	<0.1	<0.1	<0.1	0.1
Russia[b]	3.1	4.8	2.5	3.4	7.5	3.4
Total	*9.7*	*11.5*	*11.7*	*14.8*	*19.7*	*16.5*

[a] Ref. 24.
[b] Sales.

Table 15. Rhodium Demand by Region, t[a]

Region	1987	1990	1993	1996	1997	1998
Western Europe	2.0	3.0	3.8	4.8	5.1	5.7
Japan	2.6	3.6	2.1	2.0	2.2	2.3
North America	4.0	4.7	4.0	5.3	4.0	5.5
rest of world	0.6	0.9	1.3	2.6	3.0	2.6
Total	*9.2*	*12.2*	*11.2*	*14.6*	*14.3*	*16.1*

[a] Ref. 24.

Table 16. Rhodium Demand by Application, t[a]

Industry	1987	1990	1993	1996	1997	1998
autocatalyst	7.0	10.4	11.1	13.2	12.9	15.2
gross recovery	0.1	0.4	0.9	1.4	1.5	1.8
chemical	0.7	0.8	0.3	0.7	1.1	1.0
electrical	0.4	0.4	0.2	0.3	0.3	0.3
glass	0.4	0.5	0.1	1.6	1.3	1.1
						0.3
other	0.8	0.5	0.4	0.3	0.3	
Total	*9.2*	*12.2*	*11.2*	*14.6*	*14.3*	*16.1*

[a] Ref. 24.

Table 17. Ruthenium Demand by Application, t[a]

Industry	*1987*	*1990*	*1993*	*1996*	*1997*	*1998*
electrical	2.7	2.7	3.9	4.9	5.5	5.7
process catalyst	1.8	1.9	1.7	3.8	2.6	2.7
electrochemical			2.1	2.0	2.3	
other	0.6	0.1	0.1	0.9	1.1	0.9
Total	*5.1*	*4.7*	*5.7*	*11.7*	*11.2*	*11.6*

[a] Ref. 24.

Table 18. Iridium Demand by Application, t[a, b]

Industry	1987	1990	1993	1996	1997	1998
process catalyst	ND	ND	ND	0.8	0.4	0.1
electrochemical	ND	ND	ND	0.8	0.8	0.9
automotive	ND	ND	ND	1.1	1.9	1.1
other	ND	ND	ND	1.0	0.9	1.1
Total	*1.1*	*0.8*	*1.0*	*3.7*	*4.0*	*3.2*

[a] Ref. 24.
[b] ND = not disclosed.

There is no price given for osmium because demand is too low. Price data was compiled from *Platinum* and from *The Precious Metals Report* (23, 24).

Total global demand for platinum reached 166.3 metric tons in 1998, up 60% since 1987. In terms of tonnage, platinum's two principal uses are in jewelery and in automotive catalysts, which now account for 44% and 34% of use, respectively. Growth in the use of PGMs in automotive catalysts has been driven by the introduction of emissions legislation, which has become increasingly stringent over the last two decades. This is discussed in more detail in the uses section.

As can be seen in Figure 4, the price of palladium has soared over recent years, and it is no longer significantly cheaper than platinum. This has been due to record demand, particularly from the automotive industry, and also to erratic supply from the world's leading producer, Russia. For the principal uses, demand has continued to grow rapidly, despite unpredictable supplies and higher prices.

Palladium demand reached record levels of 254 t in 1998. Demand was up nearly 10% compared to the previous year, and up 157% since 1987. The three main uses of palladium are in autocatalysts, electrical and electronic applications, and in dental alloys. Use of palladium in autocatalysts has increased one-hundredfold over the decade, due to the introduction of palladium-containing catalysts to an increasing number of gasoline vehicles, where it has either replaced or supplemented the use of platinum. Palladium use in electronics and electrical applications has been driven by consumer demand for products such as mobile phones and computers.

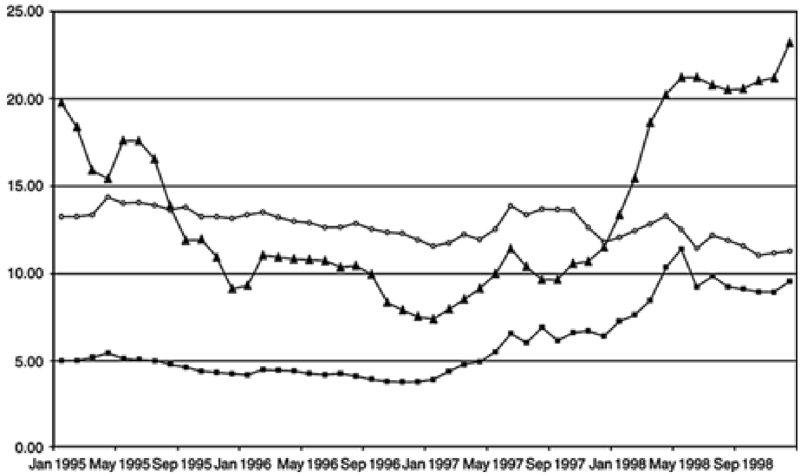

Fig. 4. Average monthly prices for platinum, palladium, rhodium in $/g

World demand for palladium alloys in dentistry has grown steadily, following safety concerns over base metal alloys, and because of cost benefits over gold.

By far the largest use of rhodium is in the autocatalyst industry, which accounds for around 80% of rhodium demand. Rhodium is also used in the glass industry, in thermocouples for the steel and semiconductor industries, and as a chemical catalyst, eg, in the production of acetic acid and oxo-alcohols.

4.3. Other PGMs

Detailed supply and demand figures by region are not available for ruthenium and iridium. However, demand by application is shown in Table 17 and 18. Demand for osmium is very low (probably less than 100 kg annually), although no detailed figures are available.

The main applications of ruthenium are in the chemical and electronics industry. Demand for ruthenium process catalysts has increased recently, following the introduction of the Kellogg Advanced Ammonia Process (see Uses). Ruthenium coated electrodes are used in the production of chlorine. Ruthenium-based resistors are found in many electronic circuits.

Iridium is used in some process catalysts, including a new acetic acid process, and like ruthenium, it is used in electrodes for the chlor-alkali industry. In the automotive industry, iridium is used in spark plugs. In the electronics industry, iridium crucibles are used to grow synthetic single crystals for use in lasers. About 0.1 tons of iridium are used in crucibles each year, and are included in “other” in Table 18.

5. Analysis

Like the refining of the PGMs, the analysis is complicated by the chemical similarity of the metals. The techniques used depend on the elements present and their concentration in the sample. For some low grade samples, analysis is preceded by a concentration stage using fire assay with collection into a lead or nickel sulfide button. The individual metals can then be determined.

Colorimetric and fluorimetric techniques are sensitive and accurate but have generally been superseded by other methods in specialist analytical laboratories. Gravimetric techniques are still widely used for all the PGMs but require correct preseparation procedures. The examination of solid materials is carried out by using either x-ray fluorescence spectrometry, where the use of matrix-matched standards is essential, or dc-arc spectrography and spectrometry, where setup, sampling, and standardization are all element-specific. The most widely used method for determining low concentrations of the PGMs in solution is atomic absorption spectrometry, which is useful for single element determinations but slow and laborious for multiple elements. Plasma emission spectrometry is the method of choice for rapid multielement analysis. Detection limits are 0.1–10 ppm, depending on the element. For two-orders-of-magnitude lower detection limits, the plasma mass spectrometer is used in specialist PGM laboratories.

6. Environmental Concerns

In recent years, an increasing number of papers has been published on all aspects of platinum in the environment. Many of these papers focus on possible emissions from autocatalysts, but to date, there is little consistency. A thorough review of the topic is given in Ref. 25.

Estimates of platinum emissions from autocatalysts very widely, from 0.01 to 6 μg/km. Loss of 5% of the platinum from a catalyst over 160,000 km would equate to a loss of about 1 μg/km. To put this figure into perspective, a car running on leaded fuel emits over 14,000 μg of lead per km. Although levels of platinum in the air are measureable, they are many orders of magnitude less than occupational exposure standards.

Platinum also enters the environment through its use in cancer treatment, ending up as sewage sludge. Some reports have suggested that small amounts of platinum may be lost during the oxidation of ammonia to produce nitric acid. Platinum can also enter the environment from natural sources, eg, cosmic dust.

7. Health and Safety Factors

In bulk metallic form, the PGMs are not hazardous to health. However, like many other metals in finely divided form, PGM powders can be hazardous to handle. Powdered platinum is a powerful catalyst and is liable to ignite combustible materials. Powdered iridium can ignite in air and palladium dust is combustible.

Table 19 shows the relevant exposure limits for platinum, rhodium and their compounds in the United State and the United Kingdom.

8. Uses

8.1. Catalytic Applications

The PGMs are widely used as catalysts for many reactions in the chemical industry, including hydrogenation, oxidation, dehydrogenation, isomerization, cyclization and carbon–carbon bond formation. Table 20 shows the application of the individual PGMs for particular reactions.

In the chemical industry the choice between base metal or PGM catalyst ultimately depends on process economics. In developing improved catalysts, improved activity and selectivity towards a particular reaction is sought. However, the reaction conditions under which a catalyst is active also have important applications for the process. For example, milder reaction conditions (lower temperatures and pressures) decrease overall capital investment costs.

The following general points can be made about the advantages and disadvantages of base metal or pgm catalysts:

Table 19. Occupational Exposure Limits for the PGMs[a]

Metal or Compound	Relevant Standard or Limit	
United Kingdom[a]		
Platinum metal	Occupational exposure standard	5 mg/m^3 (8 h TWA)b,c
soluble Pt compounds (except certain halogeno compounds)	Occupational Exposure Standard	0.002 mg/m^3 (as Pt) (8 h TWA)
halogeno Pt compounds (complex coordination compounds in which the Pt atom is directly coordinated to halide groups)	Maximum Exposure Limit	0.002 mg/m^3 (as Pt) (8 h TWA)
rhodium metal, fume and dust	Occupational Exposure Standard	0.1 mg/m^3 (8 h TWA) 0.3 mg/m^3 (15-min STEL)
soluble Rh salts	Occupational Exposure Standard	0.001 mg/m^3 (as Rh) (8 h TWA) 0.003 mg/m^3 (as Rh) (15-min STEL)
United States[d]		
platinum metal	Threshold Limit Value	1 mg/m^3 (8 h TWA)
soluble Pt salts	Threshold Limit Value	0.002 mg/m^3 (as Pt) (8 h TWA)
rhodium metal	Threshold Limit Value	1 mg/m^3 (8 h TWA)
insoluble Rh compounds	Threshold Limit Value	1 mg/m^3 (as Rh) (8 h TWA)
soluble Rh compounds	Threshold Limit Value	0.01 mg/m^3 (as Rh) (8 h TWA)
osmium tetroxide	Threshold Limit Value	0.0002 ppm (8 h TWA) 0.0006 ppm (15-min STEL)

[a] Ref. 26.

[b] TWA = time weighted average.

[c] STEL = short term exposure limit.

[d] Ref. 27.

Table 20. Catalytic Applications of PGMs

Reaction	Pt	Pd	Ru	Rh	Ir	Os
hydrogenation	●	●	●	●	●	
oxidation	●	●	●	●		
dehydrogenation	●	●				
hydrogenolysis	●	●	●			
synthesis, ammonia			●			
synthesis, methanol		●				
synthesis, hydrocarbons			●			
synthesis, acetic acid				●	●	
hydroformylation			●	●	●	
carbonylation				●		
cis-Hydroxylation						●

PGM catalysts are often more active than base-metal catalysts and allow reactors to operate under milder reaction conditions with all the associated economic benefits. However, because PGM catalysts tend to be more active, they are sometimes more prone to deactivation due to poisoning. When searching for improved catalysts it is always extremely important to subject the catalyst to real conditions for long operating times.

PGM catalysts are non toxic and non-pyrophoric, making them safe and easy to handle.

PGM catalyst manufacturers can deliver the catalyst in the appropriate state such that pretreatment by the user is not necessary.

Waste disposal is not an issue because PGM catalysts can be returned to the manufacturer for recovery and recycling (PGM recovery rates of 98–99% are usual). Base-metal catalysts are generally discarded after use.

In terms of cost, it might be imagined that base metals would always be preferred to PGMs, the raw materials typically being 100–1000 times less expensive than PGMs. However, the real cost of a PGM catalyst has to take into account the cost of the catalyst manufacturing method and the cost implications of end-of-life recycling for PGM catalysts. In many cases it turns out that PGM catalysts offer an economic, as well as a technical advantage, over base-metal alternatives.

8.1.1. Catalysis for chemical industry applications

In terms of tonnage, the PGM used in the chemical industry in greatest amount is platinum. It is used in many of the largest scale processes, including petroleum refining, nitric acid synthesis, silicone production etc. The chemical industry accounts for about 30% of global iridium consumption, and about 40% of global ruthenium demand. Palladium is used in a number of bulk chemical processes, including acetaldehyde and hydrogen peroxide production. It is also widely used as a hydrogenation catalyst in the fine chemicals industry. Processes using PGM catalysts are too numerous to list fully here; however several significant PGM catalysed processes are outlined below.

8.1.1.1. Ammonia. The majority of ammonia synthesis plants use a catalyst based on magnetite (Fe_3O_4). However, the recently introduced Kellogg Advanced Ammonia Process (KAAP) uses a Ru catalyst. This catalyst is claimed to be 20 times more active than magnetite (28), enabling the process to be operated at lower pressures and temperatures. KAAP can offer cost savings over the traditional base-metal catalyzed process in areas where electricity is expensive, and the feedstock, natural gas, is plentiful and cheap. Once installed, the Ru catalyst has a long life, with only small in-process losses. To date, KAAP technology has been installed in only a few new ammonia plants (in Trinidad, Canada and Australia).

8.1.1.2. Nitric Acid. Nitric acid (qv), is made industrially by the catalytic oxidation of ammonia (qv). The oxidation catalyst is usually a platinum alloy gauze, containing 5 to 10% of rhodium, or optionally 5% palladium. Typically, a catalyst pack contains up to 36 gauzes and requires 25 kg of Pt–10% Rh alloy (worth about $300,000 at current prices) (29, 30). Catalyst life is about 50–300 days, before recovery is required. The catalyst is hence a major cost component of the nitric acid process.

In the early 1990s knitted gauzes began to replace woven ones, and by 1994, 80% of one major manufacturer's customers were using knitted gauzes (30). Knitted gauzes have proven to offer significant benefits, including: faster gauze fabrication (less PGM stocks tied up in the knitting process), stronger, more flexible gauzes which are less prone to damage, greater surface area for catalysis and increased ammonia conversion efficiency, lower metal losses and extended campaign lengths. Nitric acid plants also require a palladium–gold gauze, which is placed below the platinum gauze to recover platinum lost through mechanical abrasion and evaporation of PtO_2.

8.1.1.3. N-Aldehydes. The oxo process for the conversion of alkenes to *n*-aldehydes use is carried out globally on a scale of about 7×10^6 t/yr. A homogeneous Rh catalyst has replaced the conventional Co catalyst in at least 40% of hydroformylation plants worldwide.

8.1.1.4. Acetic Acid. In the 1960s, Monsanto discovered that a Rh/iodine catalyst was significantly more active for the carbonylation of methanol to acetic acid than the previously used Co/iodine catalyst. By 1991, about 55% of acetic acid capacity worldwide used the Rh technology (31). Although this has proven to be the most successful acetic acid process on economic grounds, limited availability of Rh compels it to operate in the most loss-free way possible.

In a recent development, BP has launched its Cativa technology for the carbonylation of methanol, for which it developed an iridium catalyst. This catalyst can tolerate a wider range of process conditions than the Rh catalyst and allows higher rates of reaction. It can be retrofitted into existing plants, and increases capacity by over 30% by speeding up the slowest step in the process (32).

The Hoechst/Halcon process for the carbonylation of methyl acetate or dimethyl ether to acetic anhydride also uses a homogeneous Rh catalyst (33). BP also operates a Rh-catalysed carbonylation of methanol/methyl acetate mixtures. Yields of acetic acid and acetic anydride in ratios between 40:60 and 60:40 are obtained, which correspond to market demand (34).

8.1.1.5. Hydrogen Peroxide. Most hydrogen peroxide (ca 95%) is manufactured using the anthraquinone process, which requires a palladium catalyst. The palladium hydrogenation catalyst can be on a carrier, as a gauze or in suspension.

8.1.1.6. Purified Terephthalic Acid. Palladium catalysts are required to manufacture purified terephthalic acid, which is used to manufacture polyester fiber for the textile industry, and polythylene terephthalate resins for packaging materials.

8.1.1.7. Silicones. For many years, platinum catalysts have been widely used for cross-linking silicone polymers and for the preparation of functionally substituted silane monomers. The catalyst used is often a Pt(0) complex containing vinyl siloxane ligands. Karstedt's catalyst (chloroplatinic acid in reaction with divinyltetramethyldisiloxane) is one of the most widely used (35).

8.1.1.8. Acetaldehyde. The most important industrial use of a palladium catalyst is the Wacker-Hoechst process for the partial oxidation of ethylene to acetaldehyde. In 1991, worldwide capacity for acetaldehyde was about 2.6×10^6 t/yr and currently the Wacker-Hoechst process accounts for about 85% of this capacity (36). The catalyst is a two component system: catalytic amounts of Pd(II) are used as an oxidising agent, while an excess of a copper chloride salt acts as a redox system to reoxidise Pd(O) to Pd(2+).

8.1.1.9. Vinyl Acetate. Vinyl acetate can be produced by the acetoxylation of ethylene with acetic acid in a gas phase process with a Pd or Pd acetate catalyst. Variants are known as the Bayer, Hoechst and USI (now Quantum) processes, and are used to produce over 2×10^6 t/yr of vinyl acetate (37). A similar process is used for the acetoxylation of propene.

8.1.1.10. Noble Metal Anodes. PGMs are widely used as electrode materials in electrochemistry. The chlor-alkali industry uses dimensionally stable anodes (DSAs) for the electrolysis of brine to give chlorine and sodium hydroxide. These DSAs consist of a RuO_2 or IrO_2 coating on titania. Such electrodes gained rapid acceptance in the chlor-alkali industry, as they offer a very low overpotential for chlorine evolution, together with a long service life, compared to the graphite anodes previously used. The anodes used in modern membrane chlor-alkali cells are generally coated with a mixture of RuO_2 and IrO_2, have a PGM loading of 10–20 g/m^2 and a guaranteed operating life of five to eight years. The chlor-alkali industry also uses pgms for the hydrogen evolving cathodes; these typically consist of Ni with a coating of Pt–Ru.

DSAs with an IrO_2 coating are used in numerous other applications such as cathodic protection, electrogalvanizing and electrowinning. Platinized titanium anodes are widely used for cathodic protection in seawater environments. Iridium–platinum electrodes are used in the electrochemical production of chlorate (38).

8.1.1.11. Fine Chemicals. PGMs and their complexes are widely used in the fine chemicals industry. PGM catalysts (especially palladium or platinum) are routinely used to catalyze hydrogenation reactions in the manufacture of many products.

Examples include: The antiparasitic agent, Invermectin, used to treat riverblindness in the third world, is prepared by rhodium catalyzed hydrogenation of avermectin at ambient temperature and pressure. The reaction is highly selective, and gives high yields of product. Ibuprofen can be made in a three-stage synthesis involving the palladium catalyzed carbonylation of 1-(4-isobutylphenyl)ethanol. This Pd-catalyzed route, developed by Boots Hoechst Celanese, has replaced the traditional, relatively inefficient, noncatalyzed six-step process.

In the hydrogenation of glucose to sorbitol, the nickel hydrogenation catalyst is replaced with a supported ruthenium/carbon catalyst. The operating pressure can be reduced from about $40–70\times10^5$Pa to 25×10^5Pa and the reaction temperature from 130–150°C to 120°C. Nickel-contaminated wastewater is avoided.

Osmium tetroxide is used as an oxidation catalyst, particularly for the oxidation of olefins to *cis*-diols.

One area of increasing importance is the development of single enantiomer forms of pharmaceuticals, agrochemicals, and other fine chemicals. PGM catalysts with chiral ligands play an important role in the production of single enantiomer chemicals, giving good enantioselectivities and being easily scaleable to full production. Commercial examples include the use of a chiral iridium catalyst by Novartis to produce the herbicide Metolachlor.

8.1.1.12. New Applications. Novel applications of PGMs are appearing all the time. One such area is a novel palladium catalyzed process for copolymerizing olefins with polar monomers to give polyketones which can be used as engineering thermoplastics with superior properties. Shell is operating such a process for the production of the engineering thermoplastic Carilon.

8.1.1.13. Petroleum. The petroleum industry uses PGMs as catalysts in catalytic reforming, hydrogenation, and isomerization reactions. They are also used as promoters in other reactions. The reforming process is carried out using a special bifunctional catalyst, such as $Pt/Al_2O_3{\cdot}SiO_2$ (Platforming process) or $Pt\text{-}Re/Al_2O_3{\cdot}SiO_2$ (Rheniforming process). The former (UOP process) is currently used in at least 100 plants worldwide, while the latter (Chevron process) is used in more than 70 plants (39).

A platinum–aluminum silicate catalyst is also used for the isomerization of C8 aromatics (40). The advantages of the PGM vs non-PGM catalyzed route are long catalyst life and low losses of aromatics from disproportionation and transalkylation. These advantages more than offset the increased initial cost of catalyst.

UOP operates a process for the dehydrogenation of paraffins to produce olefins. This uses a Pt/alumina catalyst. Olefins produced using this process are signifiantly cheaper than olefins produced using the Ziegler or ethylene oligomerization processes, but cannot compete in terms of linearity. However, at least 25 plants are operating with this technology.

A newer application of platinum in refining is the dearomatization of diesel fuel. Introduction of this process was initially driven by legislation in California and Sweden requiring the reduction of aromatics and sulfur in diesel; now however, dearomatisation units are also being installed on economic grounds.

8.1.2. Automotive Emission Control catalysts (Autocatalysts)

Many countries around the world have recognized the environmental problems caused by car exhaust emissions and have introduced legislation to combat the problem. The specified limits have been achieved by two main approaches: modified engine designs to decrease engine-out emissions, and exhaust aftertreatment by heterogeneous catalysts. The development of emission standards and improved catalysts is a continuing process.

8.1.2.1. Autocatalyst Technology. The first type of autocatalyst to be developed was the oxidation catalyst. This is effective at oxidizing carbon monoxide (CO) and hydrocarbons (HC) to carbon dioxide and water, and contains platinum, palladium or a mixture of both metals.

Oxidation catalysts are unable to control nitrogen oxide (NO_x) emissions. Since the early 1980s, the primary emission control system for four-stroke passenger car gasoline engines has been the three-way catalyst. This catalyst system is capable of oxidizing CO and HC and simultaneously reducing NO_x. The three-way converter operates efficiently only close to the stoichiometric air–fuel ratio. Therefore the engine has to function at around the stoichiometric air–fuel ratio and this is controlled by means of a feedback sensor placed in the exhaust system. In addition, mass air sensors and electronic fuel injection systems allow precise air-fuel metering.

Three-way catalysts are manufactured by dispersing PGMs onto ceramic or metal honeycomb supports. High surface areas are achieved by coating the support with an alumina-based washcoat, into which pgms

Table 21. PGM use in Autocatalyst Applications, t

PGM	1993	1994	1995	1996	1997	1998
platinum	52.9	58.2	57.4	58.5	56.9	56.9
palladium	21.9	30.3	56.0	73.4	99.5	139.0
rhodium	11.1	11.8	14.4	13.2	13.0	15.2
Total	*85.9*	*100.3*	*127.8*	*145.1*	*169.4*	*211.1*

are subsequently impregnated. Three-way catalysts designed to meet 1997 U.S. LEV standards remove 98% of engine-out hydrocarbons and 95% of carbon monoxide and NO_x.

Platinum, palladium, and rhodium display different, but related properties. None of the three metals alone has the desired activity to catalyze all of the complex reactions that are necessary for the removal of pollutants in a three-way catalyst. Platinum is the most active of the three metals for converting CO and HC and is least susceptible to poisoning by lead, sulfur, and other impurities in the fuel. It is quick to start working from cold but does not show much ability to reduce NO_x. Rhodium has a very high NO_x reduction activity and is good at converting the other pollutants, but its availability is more limited. Palladium shows excellent low temperature performance and high temperature resistance, coupled with high HC conversion capability but is more easily poisoned particularly by fuel-derived sulfur and lead species than platinum.

Three-way catalysts based on palladium, either alone or in combination with rhodium and platinum, are now the most widely used catalyst system for treating emissions from gasoline engines. Palladium–rhodium formulations are particularly suited to close-coupled applications in markets where the availability of unleaded fuel is good and where any trace lead levels are low. Incorporation of some platinum to give a platinum:palladium:rhodium trimetal combination gives improved lead tolerance and is preferred in cooler, underfloor locations where the possibility of poisoning by residual lead still exists. A further advantage of high-palladium content catalysts is that they tend to generate less hydrogen sulfide under rich conditions.

8.1.2.2. PGM in Autocatalysts. In the past five years, palladium has become the most widely used pgm in autocatalyst applications, as shown in Table 21. The increase in palladium use in 1998 was driven by the implementation of the NLEV program in the U.S. with automakers supplying vehicles equipped with palladium-rich catalyst systems with relatively high loadings to meet the tighter hydrocarbon limits. Palladium-based three-way catalysts in close-coupled positions to produce fast light-off are now widely used in gasoline applications.

In Europe also there has been a continuous trend towards the use of palladium-rich catalysts since 1993. In 1998, palladium demand increased further because of a shift towards palladium-rich catalysts on gasoline cars and the use of higher loadings in anticipation of Stage III European emissions standards.

Platinum demand in autocatalysts has remained relatively stable over the past few years. However these numbers mask a more subtle change in the demand pattern. Since 1997, all new diesel vehicles sold in Europe have carried platinum autocatalysts in order to meet Stage II EU emissions limits. In 1998, owing to rising sales of diesel vehicles, this application outweighed a decline in the use of platinum on catalysts for gasoline cars where palladium-rich catalysts are now preferred. European Stage III legislation, formally enforced from 2000, is likely to require higher platinum loadings on catalysts for diesel vehicles. Some manufacturers have already started to increase loadings in anticipation of the introduction of this legislation. Most U.S. automotive manufacturers continue to use platinum-based catalysts to meet current Federal standards. Consumption of platinum was supported by the growth in light duty truck sales, which generally require larger catalysts containing more pgms.

8.1.2.3. New Developments. Areas of active development include control of cold start emissions (42), diesel exhaust aftertreatment (43), catalysts for lean burn gasoline engines (44–46), particulate control (47, 48), and control of emissions from two-stroke engines. These areas all involve PGM catalyst development.

8.1.3. Industrial and Stationary Source Emission Catalysts

Catalytic incineration is widely used in many industries to destroy fumes and odors caused by the presence of volatile organic compounds (VOCs). VOC emissions occur in a wide range of industries. In March 1999, the European Union passed Council Directive 1999/13/EC limiting emissions of VOCs in many industries. VOCs are most effectively destroyed by incineration, which involves oxidation of the hydrocarbons, hydrocarbon containing materials and carbon monoxide. By incorporating a suitable oxidation catalyst into the incineration system, both the reaction rate is increased and the energy required for the reaction to occur is significantly decreased. PGM-based catalysts are particularly suitable for this application as they are highly active oxidation catalysts, as well as being chemically and physically stable. The PGM is typically dispersed on a thin-walled honeycomb support, similar to that used in automotive catalysis. Once installed, they are long lasting. A single charge of catalyst destroys VOCs from a process for several years.

PGM catalysts can also be applied to the control of emissions from stationary internal combustion engines and gas turbines. Catalysts have been designed to treat carbon monoxide, unburned hydrocarbons and nitrogen oxides in the exhaust, which arise as a result of incomplete combustion. Over half of all emissions of synthetic nitrogen oxides come from stationary sources, including power station boilers, industrial boilers, stationary internal combustion engines. Either selective catalytic reduction (SCR) or nonselective catalytic reduction (NSCR) can be used, both of which may require PGM catalysts (49).

NSCR uses a three-way catalyst to remove nitrogen oxides, carbon monoxide and hydrocarbons from exhaust gas streams with a low oxygen content simultaneously, eg, nitric acid plant tail gas, or rich running gas-fueled engine exhaust. The catalysts used are similar to the three-way catalysts used in the automotive industry.

SCR is used to remove nitrogen oxides from exhaust gases with high oxygen contents. These conditions are found in a wide range of applications, including boiler-flue gas, furnace emissions, gas-turbine exhaust, lean-operating gas fueled engines, etc. A reducing agent, often ammonia, is added to the gas stream, and this enables the nitrogen oxides to be reduced selectively in the presence of an oxidizing environment. The catalyst can be either platinum or a base metal oxide such as titania or vanadia. Platinum is particularly efficient at low temperatures between 180 and 240°C, but must not be operated at temperatures that allow the formation of ammonium nitrate or nitrite, because of the explosion hazard.

8.1.4. Fuel Cells

Fuel cells (qv) are electrochemical devices that convert the chemical energy of a fuel (usually hydrogen) directly into electrical and thermal energy. The fuel cell is an environmentally clean method of power generation (qv) as it is more efficient than most other energy conversion systems and because the main by-product is pure water.

A fuel cell contains two electrodes, one of which is supplied with a fuel such as hydrogen (the anode), and the other with oxygen (the cathode). The electrodes are separated by an electrolyte. Fuel cells are usually classified by the type of electrolyte used in the cell. The low-temperature fuel cells phosphoric acid fuel cells (PAFC); alkaline fuel cells (AFC); proton exchange membrane fuel cells (PEMFC); and direct methanol fuel cells (DMFC).

All of these low temperature fuel cells use catalyzed electrodes. In PAFC, phosphoric acid is the electrolyte and the electrodes are coated with platinum black or platinum supported on carbon. Platinum promotes the electrochemical reaction by weakly adsorbing hydrogen and oxygen on the metal surface this enables rapid formation and breaking of the metal–hydrogen and metal–oxygen bonds.

At the heart of a PEMFC is the Membrane Electrode Assembly (MEA) which has three main components: two electrodes, each consisting of a carbon-based substrate coated with a platinum catalyst, and a solid electrolyte in the form of a polymer membrane.

In the late-1980s, considerable interest began to be shown in PEMFC for transport applications. Ballard Power Systems in Canada pioneered research into PEMFC as an alternative to batteries for electric vehicles, a market opportunity created by Californian emissions legislation in 1990, which included a mandate for zero emission vehicles (ZEV). PEMFC are especially suitable for transport applications because they operate at comparatively low temperatures, allow a rapid start-up from cold, and a high power density, making them relatively compact.

An important milestone was achieved in 1995 when Ballard Power Systems and Daimler-Benz unveiled a PEMFC stack with a power density of 1 kW/L. This represented a five-fold improvement in performance in five years. Progress was also made in reducing platinum loadings on PEMFC fuel cell catalysts, an important factor in enabling cells to be produced at a competitive price.

The first full-scale demonstration of a fuel cell powered vehicle took place in 1993, with Ballard's prototype bus powered by PEMFC.

Several companies have built cars powered by fuel cells. Daimler-Benz, using Ballard technology, has developed several PEMFC cars, the most recent of which has demonstrated that fuel cells are now sufficiently compact to fit into a small car. Toyota has shown fuel cell versions of its RAV4 multipurpose vehicle, powered by its own PEMFC technology. Several other car manufacturers have also launched prototype fuel cell vehicles.

In a vehicle, the fuel cell stack must be incorporated into a system, which provides a source of hydrogen fuel to the cell, and then uses the electricity generated to drive a motor. The hydrogen can either be stored in tanks, or generated through the reforming of a liquid fuel such a methanol or gasoline. Liquid fuels are more practical because they have a greater energy density, thus extending the range of the vehicle, and refuelling is simpler. However on-board reforming presents a number of technical and engineering challenges. Fuel processing and gas purification equipment must be incorporated into the vehicle, and the system must be capable of delivering varying amounts of hydrogen according to the demands of the fuel cell. PGM catalysts are also used in these applications and are reviewed in Ref. 50.

The fuel cell is a versatile, efficient, and clean technology. The only by-product of the fuel cell reaction itself is pure water, although very low emissions may be generated during the reforming of methanol or gasoline to produce hydrogen. Fuel cell cars are therefore considered Equivalent Zero Emission Vehicles (EZEV).

8.1.5. Fuel Cell Research

To achieve many of the benefits described above, the cost of the fuel cell stack must be reduced. This goal is the focus of many research programs around the world. Areas of particular activity include lowering platinum catalyst loadings in the latest stack designs, the development of lower cost membrane electrolytes, the design of alternative bipolar field-flow plates, and the introduction of mass production technology. These areas are reviewed fully in Ref. 51.

The loading of platinum black on the electrodes used in typical Ballard Mark V type stacks is 4.0 mg/cm^2. At operating cell potentials of 0.75–0.65V, the platinum black loading corresponds to 26.7–16.0 g Pt/kW of power output. Comparison with target stack costs show that these platinum loadings need to be reduced if the PEMFC is to be developed as a commercially viable product. When pure hydrogen is used as the fuel almost all of the performance losses occur at the cathode, because of the slower kinetics of the oxygen reduction reaction. Despite many studies of this reaction in the PEMFC and other types of fuel cell, platinum-based electrocatalysts remain the only practical catalyst materials, since they combine both activity and stability in the fuel cell environment. At the anode, losses in cell potential are usually small (<50 mV at 2.0 A/cm^2) because of the extremely facile nature of the hydrogen oxidation reaction on platinum-based catalysts.

Several research groups, including Los Alamos National Laboratory (52, 53) and Texas A&M University (54), have demonstrated very high cell performances from PEMFCs operating on hydrogen/air at substantially lower platinum cathode loadings than the 4.0 mg/cm^2 used in the Mark V stacks.

The Los Alamos and Texas A&M have reported performances comparable to platinum black based cathodes, but with cathode catalyst loadings of 0.12 mg Pt/cm^2 and 0.05 mg Pt/cm^2, respectively. The noble metal usage is reduced to less than 0.4 g Pt/kW of power output at operating cell potentials of 0.75–0.65 V.

Other methods of achieving high-performance cathodes with low platinum loadings have been demonstrated. This includes work by PSI Technology (55) using carbon black/polymer electrodes onto which Pr a loadings as low as 0.05 mg cm has been electrodeposited. Other groups have deposited the platinum catalyst directly into the polymer membrane electrolyte by chemical reduction of platinum salt solutions (56). Loadings deposited in this way tend to be higher than with other methods (>1 mg Pt/cm^2). It would appear that platinum can be isolated within the membrane in regions where it cannot be contacted electronically. This, coupled with the much lower platinum dispersions achieved on the membrane, has meant that the effective catalyst surface areas are inferior to those in elctrodes employing carbon-supported platinum catalysts.

The success in reducing platinum loadings has led a number of industrial and academic groups to focus on mass production methods suitable for elctrodes and MEAs. Los Alamos National Laboratory has examined the concept of ink-jet printing the electrodes (57), Texas A&M University have investigated spraying and rolling of the catalyst layers (58). A major target of the joint program between Ballard Power Systems and Johnson Matthey has been the development, for full size PEMFC stack hardware, of low platinum loading electrodes prepared in high volume. An electrode manufacturing process based on screen printing has been developed (59) and a small pilot-plant established at Johnson Matthey.

For high volume production it is undesirable to use organic solutions of Nafion. There would be considerable health and safety problems involved in the handling of large volumes of organic solvents in a production environment. There is also the possibility of interaction between the solvents and the high surface area platinum catalysts, which could result in the formation of organic by-products in the inks, and with high solvent concentration, the risk of combustion (60). A method has been developed to remove the alcohols from 5 wt % Nafion solutions to give an essentially aqueous Nafion polymer solution which is now used for routine manufacture of electrodes with catalyst loadings of 0.1–1.0 mg Pt/cm^2 (60).

8.2. Medical and Dental Applications

Two platinum complexes, cisplatin (cis[$PtCl_2(NH_3)_2$) and carboplatin (diammine (1,1-cyclobutanedicarboxylato) platinum (II)) are approved for the treatment of cancers in humans (see Chemotherapeutics, anticancer; Plantinum-group metal compounds). The compounds are particularly effective against testicular cencer, where a long-term cure is effected in more than 90% of patients (61). They have also been shown to be effective in the treatment of ovarian, head and neck, bladder, lung, prostate and cervical tumors. The first-generation drug, cisplatin, was approved in the 1970s although side effects include kidney toxicity, nausea and vomiting, myelosuppression, and hearing loss. A second generation drug, Carboplatin, approved in the UK in 1986, gives good antitumor activity, but with significantly decreased side effects.

PGMs are used wide range of medical devices, components, and implants. Key properties that are beneficial in these applications are biocompatibility, corrosion resistance, ease of working, and radiopacity. The market for such devices and implants is most developed in the United States, followed by Europe.

Platinum–iridium alloy electrodes are components of pacemakers which are used to correct slow or irregular heartbeats. Permanent pacemakers are implanted in the armpit and linked to the heart with leads finishing with two platinum electrodes. Platinum-based electrodes are also used in defibrillators. Many catheters incorporate platinum marker bands or guidewire. The radiopacity of the platinum makes the marker band or guidewire visible under x-ray, and helps the surgeon guide the catheter to the treatment site. Balloon angioplasty the guidewire often tip made of a platinum–tungsten alloy, ensuring it is visible under x-ray examination. Electrophysiology catheters for the treatment of arrhythmia or irregular heartbeat, contain platinum electrodes and marked bands. Radioactive ^{192}Ir wire sheathed in platinum can be implanted in the body to deliver doses of radiation for cancer therapy. In this example, the radiopaque property of the platinum shields healthy tissue from the radiation, while the exposed iridium tip irradiates the tumor. Platinum Guglielmi coils can be used to treat aneurysms. Soft platinum wire is threaded into the aneurysm through the femoral artery via a microcatheter. The platinum wire coils to form a mass filling the bulge in the aneurysm, so that blood can no longer circulate within it. The technique received FDA approval in 1995, and is a minimally invasive alternative to surgical clipping, a major operation that involves opening the skull.

About 38 tons of palladium were used in dental alloys in 1998. Alloys containing at leat 80% palladium are widely used as alternatives to base metal alloys in the manufacture of crowns and bridges, and in the replacement of lost or damaged teeth. (see Dental materials).

Thin rhodium foils of less than 18 micron thickness are used as filters in mammography machines. The use of such filters enables the safe use of higher doses of radiation to give better image resolution and therefore increased diagnostic accuracy.

One of the main uses of osmium tetroxide is as a biological stain, particularly for preparing samples for electron microscopy. It is unique in that it both fixes and stains biological material.

8.3. High-Temperature Applications

The exceptional mechanical and corrosion/oxidation resistant properties of PGMs, which are particularly pronounced at elevated temperatures, have led to a substantial number of applications for the PGMs and their alloys in high temperature process industries. A large use of platinum and platinum–rhodium alloys is in equipment for use in the glass industry, eg., as crucibles, stirrers, tubes, furnace linings, and bushings. The latter are troughs, which contain an array of nozzles in the base, through which molten glass is extruded to form glass fibers. Pt and Pt–10%Rh are very resistant to the high temperatures and corrosive conditions encountered in molten glass. Zirconia grain stabilized (ZGS) platinum and platinum–rhodium alloys further increase the stability and the operating life.

In applications where it is not technically or economically viable to use solid PGM alloys, coatings of PGM on the refractory ceramic substrate can be used. This allows the mechanical properties of the substrate to be combined with the corrosion resistance of the pgm, and also helps to overcome the inherent brittleness and poor thermal shock characteristics of the ceramic. Johnson Matthey's novel ACT (trademarked) coating technology (62) is being used to coat thermocouple sheaths and glass processing equipment, yielding significantly longer lifetimes.

The turbine blades of jet engines are coated with a protective layer of platinum aluminide to impart high temperature corrosion resistance. Platinum is electroplated onto the blade using P-salt or Q-salt electroplating solutions (63, 64). The platinum is then diffusion treated with aluminium vapor to form platinum aluminide. Standards for the inspection and maintenance of turbine blades have become more stringent, leading to blades being recoated several times during their lifetime. The development of more efficient, hotter engines is stimulating the use of platinum.

Tips of platinum, platinum–nickel alloy or iridium–rhodium alloy can be resistance welded to spark plug electrodes to give improved reliability and increased lifetime. These electrodes are exposed to extremely hostile environments involving spark erosion, high temperature corrosion, thermal shock and thermal fatigue. New vehicles are designed to need servicing less frequently, so the longer-lasting platinum plugs are favoured over the traditional base metal technology. In 1998, platinum-tipped spark plugs were fitted to 85% of new vehicles manufactured in the U.S. Many European manufacturers are also switching to platinum plugs. In the future it is likely that manufacturers will raise the amount platinum used per plug in order to further improve durability.

Platinum and iridium crucibles are used for the growth of high purity crystals of speciality materials such as the rare earths. Examples include gadolinium gallium garnet and yttrium aluminium garnet for use in electronic memory chips and lasers. The high melting point and oxidation resistance of the PGMs minimize contamination of the melt. Platinum laboratory apparatus is routinely used in chemical analysis.

8.4. Electronic Applications

The PGMs have a number of important and diverse applications in the electronics industry (65). Currently, the most widely used PGMs are palladium and ruthenium. Palladium or palladium–silver thick-film pastes are used in multilayer ceramic capacitors (MLCC), conductive tracks in hybrid integrated circuits, and for plating connectors and leadframes.

MLCC are used extensively in modern electronic devices. A personal computer, uses at least 150 MLCC. An MLCC consists of layers of conductive electrode material, usually palladium or palladium–silver, sandwiched between insulating ceramic wafers.

At each end of the capacitor, there is a metal sheath (the end termination, made of silver or a silver-rich palladium alloy) which connects the internal metal layers and provides a means of attaching the capacitor to the circuit board. Capacitors are made by screen-printing pads of conductive paste onto sheets of ceramic material. A layer of liquid ceramic is applied on top, and the sheet is fired in an oven. The process is repeated a number of times as a typical MLCC has between 10 and 50 electrode layers. The sheet is finally chopped into individual capacitors and the end terminations applied.

Most MLCC use palladium in the electrodes, but the palladium content varies quite widely depending on the specific manufacturing process and the type of ceramic used. Where firing temperatures are high, the electrode material normally contains a higher percentage of palladium, which has a much higher melting point than silver. In Japan, where high firing temperatures predominate, pastes tend to have a palladium content of at least 70%, and some higher value MLCC with a wide temperature tolerance are 100% palladium. Lower firing temperatures are more common in North America and here pastes contain only about 30% palladium.

Although the MLCC components themselves use only very small amounts of palladium, production is counted in billions which generates very substantial demand for the metal. However in 1998, worldwide consumption of palladium in MLCC fell by more than 20% compared with 1997. High palladium prices in 1998 made it increasingly difficult for capacitor manufacturers to offer price-competitive capacitors, particularly in lower specification applications. Nickel-based capacitors are now available from a number of manufacturers, particularly Japanese, who have made substantial progress in overcoming the technical problems associated with the firing of these base metal materials. In addition, further miniaturization and the use of thinner electrode layers has enabled manufacturers in all parts of the world to reduce the average weight of metal in a palladium-based capacitor.

A hybrid integrated circuit (HIC) consists of a ceramic substrate on which are mounted a number of electronic components (integrated circuits, capacitors, and resistors) linked by conductive silver–palladium tracks. It is similar to a printed circuit board (PCB) but because ceramic dissipates heat more readily than the plastic base of a PCB, more components can be used in a smaller space. HIC are smaller, more durable and more heat resistant than standard PCBs, so they are favored in applications such as telecommunications, millitary hardware and engine management systems in cars. Although growth in a number of end markets has been strong, the average size of circuits has been reduced, compelling the use of narrower conductor tracks, and the palladium content of the silver-palladium inks used to form the tracks has also been reduced. As a result, consumption of palladium in HIC was steady during the second half of the 1990s.

Components inside computers are linked by connectors plated with a conductive layer of precious metal. Traditionally the metal of choice has been gold, but following advances in electroplating technology, palladium–nickel alloys are being employed as cheaper alternatives to gold. The coating is applied by passing an electric current through a palladium plating solution, using the connector pin as one of the electrodes. Typically palladium is deposited to a thickness of about 1 μm.

A principal use for ruthenium occurs in the manufacture of chip resitors which use ruthenium dioxide as the resistive material. About one half of total ruthenium demand is a result of this application, growing 5% in 1998 to 5.7 tons.

The principal use of platinum in electronic applications is in hard disks for personal computers. Increasing data storage requirements for computer applications are creatings demands for advanced magnetic and magneto-optic storage media. The disks are coated with a cobalt-base alloy with magnetic properties, which stores the individual pieces of data, or “bits”, in a series of cicular tracks. The addition of platinum enhances the magnetic qualities of the cobalt alloy, which enables data to be stored at higher densities and also improves access times. Many new drives disk use magnetoresistive (MR) head technology, in which the read and write functions are separated into two distinct heads. Some MR heads use small amounts of platinum to enhance their magnetic properties. In 1998, consumption of platinum in hard disks was just under eight tone. With the expected growth in demand for data storage, this is expected to increase to about 15 t within the next four years.

Platinum cobalt multilayers demonstrate good perpendicular magnetic anisotropy, which makes them excellent candidates for magneto-optic data storage (66).

There is considerable interest in the use of thin-film platinum silicide in silicon integrated circuit technology. Platinum silicide has low resistance and high stability, and can provide both ohmic low resistance contacts and rectifying contacts. Typically, silicide layers are formed *in-situ* by sputtering a thin platinum layer onto the silicon surface, followed by sintering. Infrared detection is another application of platinum silicide technology.

8.5. Temperature Measurement

PGM thermocouples are widely used for high temperature measurement in the glass, steel and semiconductor industries owing to their linear, high thermoelectric voltages. In the semiconductor and glass industries, permanently installed profiling thermocouples are used to control furnace temperatures. In the steel industry, disposable thermocouples give an instantaneous temperature reading before being destroyed in the furnace. Type S (Pt vs Pt–10 wt% Rh) and type R (Pt vs Pt-13 wt% Rh) are used over the temperature range 0–1450°C. Type B thermocouples (Pt-6 wt% Rh vs Pt–30 wt% Rh) operate over the range 870–1700°C. For higher temperatures, normally 1800–2000°C, an Ir vs Rh–40 wt% Ir thermocouple is available.

High purity platinum wire is used in resistance thermometers. This is primarily because of the temperature coefficient of resistance of pure platinum, which is linear over a wide temperature range. The platinum resistance thermometer is the recognized instrument for the interpolation of the International Practical Temperature Scale from -259.35°C to $+630.74^\circ$C. While such precision measurements require very high purity platinum, for most routine industrial measurements lower purity metal can be tolerated. Conventional wire-wound devices are quite fragile and this disadvantage has led to the introduction of printed resistance thermometers, which are cheap to produce and much more durable. They can be used as an inexpensive replacement for thermocouple applications in intermediate temperature applications.

8.6. Jewelry and Investment

Platinum is widely used in jewelry, particularly in Japan where it is preferred to gold. As pure platinum is too soft for jewelry applications, it is alloyed with other PGMs such as iridium or ruthenium to increase its hardness and wear resistance. A Pt–5% Ir alloy has excellent hardness and strength but has a grayish color and easily loses its surface finish and luster. These problems are overcome by the addition of palladium as a whitening agent. A 95% Pt–4.5% Pd–0.5% Ir alloy is a widely used material. Palladium is also used as a whitening agent in gold jewelry. Platinum jewelry alloys are easily workable, and readily melted and cast. However, they are difficult to machine, resulting in severe tool wear. Pure platinum (99.95%) in the form of coins and ingots is used as an investment metal.

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