European Precious Metals Conference

NEW TECHNOLOGY AND ADVANCES IN AUTOMOTIVE APPLICATIONS

The Second Eurometaux Precious Metals Conference, organised by members of the European precious metals industry, was held in Lisbon from 10th to 12th May, 1995. The industry is seeing the spread of environmental legislation which is imposing new constraints on it, but at the same time is also creating opportunities for the development of new technologies and uses. Around 200 representatives from European and other noble metals industries attended the conference. Here we present a selective review of some of the platiniferous work reported at the sessions on advances in precious metals applications, and especially on recent innovation in automotive applications.

Precious Metals Applications

A paper by H. H. Beyer of Degussa reported on a method for surface hardening platinum, by the use of boron for jewellery applications. A hardened layer suitable for polishing is produced when a boriding agent diffuses into platinum during heating for three hours at 600°C. Beyer also outlined the use of electroforming for the production of thinner, hollow, intricate jewellery. A system where platinum is electroformed using titanium electrodes at 75°C is now being tested and is expected to become commercially available soon.

Palladium in Contact Bonding

The use of palladium and palladium alloys for contact and bonding applications was discussed by J. Wachter of W. C. Heraeus. For many years palladium has been used in the manufacture of switch contacts. When palladium only is used, a brown powder is formed during operation in an organic gas environment.

The substitution of silver to form a 70 per cent palladium-30 per cent silver alloy significantly reduces the powder formation, and more recently the introduction of copper to form a three-way alloy has increased the tensile properties of the alloy. If palladium-only contacts are required, the formation of brown powder can be reduced to minimal levels by the introduction of a gold film. This also serves to increase the wear resistance of the contact.

Palladium Powders in Microelectronics

A paper describing the use of palladium metal powders for microelectronics was presented by E. M. Meyer of Metalor. Palladium used in the electronics industry accounts for around 47 per cent of the total demand. Palladium is used in bonding applications via ultrasonic friction or press welding, and one of the largest bonding applications is in the production of microelectronic devices. Here layers of palladium powder are sandwiched between barium titanate to form a circuit.

Advances over the years have resulted in smaller devices requiring a continuous layer of palladium powder, which must be free of lumps. With the constant demand for yet smaller electrical devices, new methods will be required to produce finer palladium powders.

Deposition Processes

Various methods of deposition of the platinum group metals, and the components formed using these processes, were discussed by D. A. Toenshoff and R. D. Lanam, Engelhard, (EI). While salt plating is inexpensive, it is difficult to vary the substrate, and the deposit has to be relatively thick. Sputter coatings, however, which need to be only half as thick, retain the same properties as salt coatings, and can utilise many different substrates. New applications for sputter coatings include power tools coated with platinum, platinum on tungsten for the lighting industry and platinum coated wires for pacemakers.

A second process, known as the "PDC" process, described enhanced plasma and high velocity oxygen fuel coating techniques, which are used to deposit fine layers of precious metals. Such techniques are being developed towards the fabrication of finished forms. Coatings that were mentioned included platinum, iridium and platinum/rhodium.

Electroforming technology can purify the platinum group metals, as well as form complex shapes of platinum group alloys and refractory metals and has been used by EI to produce iridium crucibles. The electrolyte is a complex salt of the metals with halogenoids of alkaline metals. Electroforming takes place from the halogenoid melt under inert gas at elevated temperature, using an anode of the metal to be deposited and a shaped mandrel which determines the geometry of the final component. The advantage of this method is that it produces extremely pure metal. EI are developing this process for ruthenium and iridium products.

Iridium

A paper by D. Lupton of W. C. Heraeus and B. Fischer of Jena Polytechnic reported on the difficulties in processing iridium, due to its high rate of work hardening and the deleterious effects of small levels of contaminants segregating strongly to grain boundaries. It pointed, however, to the excellent high temperature strength of iridium, and showed its stress rupture properties at 1800°C to be comparable to those of platinum-rhodium or dispersion strengthened alloys operating at much lower temperatures.

Advanced Coating Technology

A paper by P. N. Duncan and W. G. Hall of Johnson Matthey discussed the recent development of a process for thermally depositing platinum onto a wide range of ceramic and metal substrates. This process of advanced coating technology, known as ACT™ has progressed dramatically beyond the development phase to find widescale applications notably in the glass industry. The process, which is described elsewhere in this journal, enables the best use of the surface properties of platinum, providing corrosion protection, and the mechanical strength of the substrate materials. Complex shapes can be coated, taking platinum into new areas of application where traditional cladding processes have proved impossible. The benefits to end users in the glass industry are a substantial reduction in downtime and an increased product yield, two factors which are expected to cause the ACT™ technology to grow rapidly in this field. A wide range of examples were given, showing ACT™ products before and after use in different glass types.

Automotive Applications

The session on innovation in automotive applications looked at the role of the noble metals, particularly the platinum group metals, in motor vehicles. Emission standards for motor vehicles are being set at increasingly stringent levels in a growing number of countries, and all new motor vehicles are now designed with platinum group metal catalysts to control the emissions of carbon monoxide, hydrocarbons and nitrogen oxides to these legislated levels.

The increasing growth in the use of diesel engines for passenger transport, and especially for cars in Europe, has drawn attention to the ultra fine particulates with a mean diameter of less than 10 μm, PM10s, which are emitted by diesel engines. Platinum group metals assist in the regeneration of self-cleaning particulate traps and filters to control these emissions. While carbon dioxide is not a legislated pollutant, it is the major "greenhouse" gas contributing to global warming, and increasingly more countries are encouraging the development of fuel-efficient cars, which limit the production of carbon dioxide. The growth in electronic systems designed for fuel efficiency, safety and comfort in new cars all involve precious metals for contacts, capacitors and circuitry.

Legislation and Metal Consumption

The first paper by R. A. Searles of Johnson Matthey reviewed emission standards around the world and the accelerating rate at which countries are adopting standards requiring platinum group metal catalysts for emission control. While only North America and Japan used platinum group metal catalysts between 1975 to 1985, by the end of the century all the major established and developing car markets of the world are expected to require the use of platinum group metal catalysts. This he ascribed to the growing problems caused by transport-related pollution, and the fact that the markets that develop new engines and models have tough emission limits to which all new cars are required to comply.

The new standards set in California and the Northeastern States are actively being considered for the rest of the U.S.A. and for the European Union, and these would require greater dependence on catalyst technology and more platinum group metals in each car. The technology required to satisfy these tighter regulations includes additional starter or light-off catalysts, faster acting catalysts (from a cold start) and catalysts with auxiliary heating (either electrical or by injecting a small amount of fuel).

In May 1995 it was exactly 21 years since Johnson Matthey and other manufacturers had delivered the first production quantities of autocatalysts to the U.S.A. and Japan, and 1995 is the first year in which the majority of cars in the world have catalysts. Johnson Matthey has estimated that there are now 255 million platinum group metal catalyst-equipped cars in the world, out of a total of 491 million cars, and by the year 2000 56 per cent of the car population, or 310 million cars, are expected to have catalysts.

While total demand for new platinum group metals has doubled between 1975 and 1995, their use in autocatalysts during this period has increased more than 7-fold and presently accounts for 36 per cent (3,750 thousand ounces) of all new platinum group metals produced. By 2000 the gross demand for platinum group metals for autocatalysts is predicted to increase to 5,170 thousand ounces, of which 46 per cent will be new metal.

Diesel Emissions Control

The role of platinum group metal catalysis in the control of diesel emissions was reviewed by G. Smedler of Johnson Matthey. He described the differences between petrol and diesel fuels and emphasised the twin challenge of low temperatures and lean operation for the catalyst engineer, with excess air making it impossible to apply classical three-way catalysis. However, the popularity of diesel engines has increased due to their better fuel economy and improved power and performance, and catalyst technology is being developed and applied to enhance their environmental performance.

Smedler reviewed oxidation catalysts, lean NOx and four-way catalysts and particulate filters (with catalytic regeneration). Oxidation catalysts control carbon monoxide, hydrocarbons and some of the particulates, by oxidising the volatile organic fraction. It is necessary to avoid increases in the level of sulphur trioxide in the exhaust since sulphate formation can contribute to particulate levels. Sulphate formation is minimised at exhaust temperatures of less than 400°C, but there is still a problem for engines with exhaust temperatures above 500°C and in these cases the use of the low sulphur level diesel fuels, now becoming widely available, can alleviate any environmental problems.

However, lean NOx control of the diesel engine emissions is still required. Smedler reported that a most elegant method for the decomposition of nitric oxide and other nitrogen oxides (NOx) to nitrogen and oxygen without the formation of by-products had been demonstrated on pre-reduced precious metal, particularly rhodium. However, to maintain the pre-reduced state requires the addition of selective reduction agents. Ammonia, urea and diesel fuel had been tried. Results from several systems, including platinum on alumina and copper on zeolite, were reported; these had achieved NOx conversions of 30 to 45 per cent. Progress towards overcoming the disadvantages of both systems were described.

The concept of the four-way diesel catalyst for controlling emissions of carbon monoxide, hydrocarbons, NOx and particulate was introduced. Limited ageing on experimental catalysts had shown conversions of 92 per cent, 88 per cent, 17 per cent and 37 per cent, respectively. Finally Smedler reviewed systems for filtering and destroying particulate emissions. These systems can be either active or intermittent, using burners or heaters or be passive continuous systems. Ceramic honeycomb wall flow filters are best for meeting the requirements.

The collected particulate must be destroyed by burning.

One system which had demonstrated high levels of particulate removal (and carbon monoxide and hydrocarbon oxidation) with reliable regeneration was the Johnson Matthey continuously regenerating trap, CRT. This system increases the level of nitrogen dioxide in the exhaust by oxidation of nitric oxide using a platinum catalyst. Soot is trapped on a following ceramic wall flow filter. Nitrogen dioxide, which is a powerful oxidising agent, lowers the soot/particulate oxidation temperature from 600 to 250°C. Field trials have demonstrated conversion levels for carbon monoxide, hydrocarbons and particulate of well over 90 per cent and reliable operation on a variety of engines, provided that the inlet temperature to the CRT only exceeds 250°C occasionally and that sulphur levels in the fuel are less than 100 ppm.

Three-Way Catalysts

The role of noble metals in modern three-way catalysts was reviewed by J. Mooney of EI, with respect to emissions standards, the effect on fuel quality as the level of lead is reduced and reformulated gasoline in California which contains reduced sulphur levels. He described how three-way catalyst design in North America is moving away from the original platinum/rhodium catalyst towards the use of palladium/rhodium and palladium-only systems, while in Europe platinum/rhodium and platinum/palladium/rhodium systems are mostly preferred. He said that in emerging world markets, where there was less high quality fuel, use of the platinum/rhodium three-way catalyst systems would be preferred.

After describing the operation of a three-way catalyst and the functions of the platinum and palladium as oxidation catalysts, and rhodium as a NOx reduction catalyst, he went on to discuss the mechanisms occurring on the catalyst surface. These include the role of base metal components, such as cerium, which by an oxygen storage mechanism, widened the operating window. Improved performance was achieved by separating the platinum group metals into different layers in the washcoat. He also described a unique proprietary palladium-only catalyst which could only function with the quality of fuel available in the U.S.A.

Other Automotive Uses of Platinum Group Metals

The application of precious metal contacts in automotive applications was discussed by R. Schnabl of Heraeus who reported on the significant increase in electrical systems utilising electrical contact materials in modern cars. These systems, important for reliability and safety, increasingly depend on precious metals in the contacts. Typical service requirements for robust contact materials used to switch currents of up to 100 amps and for carrying electrical signals in the milliamp and millivolt ranges are: 2.5 million switches/lifetime at temperatures up to 180°C in the presence of corrosive pollutants, with vibrations in the kilocycle range and accelerations up to 100 g. Schnabl described the use of silver/nickel and palladium/copper contacts in headlamp relays, copper contacts plated with gold or palladium/silver alloy for critical systems like airbags and brake controls. Increasingly potentiometers are used to monitor the position of throttle pedals, chokes, mirrors and seats, and require palladium-silver alloy wiper or slide contacts alloys. More demanding applications using sliding contacts in servo motors require gold or platinum alloys with copper or nickel to meet greater resistance to welding and erosion.

Recycling Catalytic Converters

The final paper in the session was presented by C. Hagelüken of Degussa, who reviewed the recycling of automotive catalyst converters. Recycled platinum, palladium and rhodium from autocatalysts already account for 18, 14 and 9 per cent, respectively, of gross demand, with most recycled platinum group metals coming from North America – an estimated 6,000 to 8,000 tons/year of autocatalyst substrate (containing 7 ton platinum, 2 ton palladium and 0.6 ton rhodium), and Japan, estimated at 1,500 to 2,000 tons/year (containing 1.7 ton platinum, 0.5 ton palladium and 0.15 ton rhodium). In Europe in 1994 only 250 tons of autocatalyst substrate were available for recycling; this contained 400 kg of platinum and 70 kg of rhodium. In Germany the number of cars sold with catalytic converters has risen from 50,000 in 1985 to 3.3 million in 1992. Hagelüken estimated that by the end of 1994 there were 40 million catalyst-equipped vehicles in Europe and this would increase by 10 million cars during 1995. At present some 8 million cars are scrapped each year, but very few are fitted with converters.

Hagelüken reviewed the system of returning scrap catalytic converters to the precious metal refiner as well as the hydrometallurgical and pyrometallurgical methods of platinum group metal recovery and separation. By the year 2000 it is anticipated that 3,500 to 4,000 tons of autocatalyst substrate should be available annually for platinum group metal recovery.

In conclusion, continuing advances in the precious metals industries, even since the first Eurometaux conference was held in 1993, together with the driving force of legislation to cope with levels of pollutants in the environment, will ensure that the interest in innovation within the European refining and fabrication industries for noble metals, remains at a high level. The Proceedings of the Conference will not be published, but papers may be obtained from Eurometaux, Av. de Broqueville, Brussels, Belgium.

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A Comprehensive Commentary on the Platinum Metals

The Platinum Group Metals: A Global Perspective

BY C. F. VERMAAK, Mintek, South Africa, 1995, 247 pages, U.S.$100.00, ISBN 0–86999–926–5

Frank Vermaak, a prominent South African geologist, has undertaken the daunting task of writing a comprehensive overview of the geology, production and consumption of the platinum group metals. His aim is to provide a down-to-earth review, accessible to a wide audience, of all aspects on the platinum group metals and to suggest future developments.

With his long experience in the platinum industry, Dr Vermaak is ideally placed to provide a thorough review of world resources and production of platinum group metals; and he devotes the first half of the book to this, outlining the occurrence of these metals in deposits across the world. He then considers output by producer, and concludes with a discussion of the technical issues involved in mining, beneficiation and refining. Much of this section concentrates upon South Africa, but there is also extensive information on platinum group metal resources and production in the U.S.A., Canada, China and Australia. This section performs a valuable service in bringing together information on smaller producers which, because of their relative insignificance in terms of total world supply, are not often reviewed elsewhere. He also includes a long discussion of platinum group metals deposits and output in Russia, although he admits that "vital data on tonnage and grade remain pretty much guesswork".

One chapter examines the marketing, distribution, trading and pricing of platinum group metals, especially up to 1992, with graphs showing the long-term price trends. Dr Vermaak also discusses trends in world consumption of platinum group metals between 1981 and 1992, providing detailed tables of usage by region and by application.

The latter part of the book provides an introduction to the many applications of the platinum group metals. One chapter discusses catalysis, and covers development and manufacture of autocatalysts and reviews environmental legislation. However, due to the extended timescale required for the production of such an ambitious treatise, Stage II European Union emissions standards and the improvements in catalyst technology which have permitted increased use of palladium in autocatalysts are not mentioned. Another chapter deals with chemical, glass and electronic applications.

Finally, Dr Vermaak examines future demand and supply of the platinum group metals. He devotes a chapter to the prospects for significant platinum usage in fuel cells; there is detailed discussion of the different types of cell, their potential applications, and progress towards commercialisation. The book ends with an examination of the social, political and economic factors influencing the outlook for demand and supply, concentrating upon the impact of the political changes in South Africa and Russia.

"The Platinum Group Metals" is a valuable addition to the literature on this subject. It should prove particularly useful for the reader seeking an expert overview of the background, geology and resources, and the uses to which the platinum group metals are put.

A.J.C.