Kunming–PM'2012

5th International Conference "Platinum Metals in the Modern Industry, Hydrogen Energy and Life Maintenance of the Future"

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The 5th international biennial conference in the series "Platinum Metals in the Modern Industry, Hydrogen Energy and Life Maintenance of the Future" was held from 15th to 19th October 2012, in Kunming, China. The conference was organised by the Kunming Institute of Precious Metals under the patronage of the International Organisation "Professor Ye. I. Rytvin Foundation" and with the support of the Non-Ferrous Metals Society of China and OJSC Supermetal, Russia. The conference was attended by 125 participants from seven countries.

The conference covered both production and a wide range of applications of the platinum group metals (pgms), including uses in the automotive, electronics, glass, dental, jewellery, hydrogen and solar energy sectors. The programme included 18 Plenary Session reports and over 40 reports were published in the conference proceedings.

The following main topics were covered during the Plenary Sessions.

Structure Control of Noble Metal Nano- and Microparticles

Professor Nanfeng Zheng (Xiamen University, China) gave a presentation on 'Multilevel Control of Noble Metal Nanostructures for Catalysis and Bio-applications'. The presentation was focused on how surface structure can optimise activity and stability for surface-dependent catalysis (e.g. ammonia synthesis and carbon monoxide (CO) oxidation) and surface-dependent electrocatalysis (e.g. fuel cells). There is a large difference in the surface energies of platinum and palladium with different surface crystal structures, and the dominant surface structure affects catalytic activity. Small adsorbents (e.g. halides, formaldehyde, carbon monoxide or amines) were used to control the metal nanostructures to prepare unique Pd and Pt nanocrystals. One of the examples discussed was Pd hexagonal nanosheets. The edge length of the hexagons increased with reaction time while the thickness remained fixed at 1.8 nm. It was proposed that the dominant surface was {111}, which gives improved electrocatalytic properties compared

with commercial Pd black as well as unique optical and photothermal effects. One of the proposed applications is in near infrared photothermal cancer therapy. Many other types of pgm nanostructures have also been synthesised by the CO adsorption method, such as tetrapod nanocrystals, nanocubes and octapods. In the oxidation of ethanol, the activity of Pt octapods was measured to be four times higher than Pt black or Pt on carbon.

Professor Xudong Sun (Northeastern University, Shenyang, China) presented a paper on 'Controllable Synthesis of Dispersed Precious Metal Powders' which reviewed achievements and problems related to preparation of dispersed precious metals powders by chemical reduction, more specifically synthesis of various morphologies, such as monodispersed spheres, single crystalline particles and nanowires. In addition to nanoparticles, microparticles of silver, gold, silver-palladium alloy, ruthenium and tungsten also have a wide range of commercial applications, such as electrode pastes and catalysts. Microparticles have two representative categories, dispersed crystalline particles and monodispersed spherical particles. Formation of dispersed crystalline particles is explained by the LaMer model (**Figure 1**) which assumes that nucleation and growth are separate. By adjusting the nucleation rate, the resulting particle sizes can be controlled. The nucleation rate is controlled by the pH while agglomeration is avoided by a high stabiliser concentration. Monodispersed spherical particles are formed by nucleation and growth to subunits from a supersaturated solution, followed by aggregation of the subunits into monodispersed spheres. The aggregation of primary particles is affected by changes in the ionic strength or pH. The presenter concluded that research on structure control of noble metal microparticles is at least as important as that on the corresponding nanoparticles.

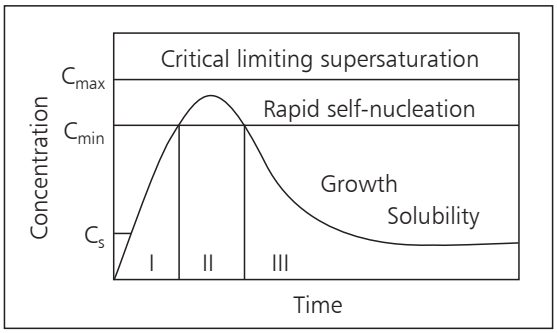

Fig. 1. LaMer model of dispersed crystalline particle formation (C_{max} = maximum concentration for nucleation, C_{min} = minimum concentration for nucleation, C_s = concentration for solubility, I = prenucleation period, II = nucleation period, III = growth period) (Image courtesy of Professor Xudong Sun, Northeastern University, China)

Tatjana Buslaeva (Lomonosov Moscow University of Fine Chemical Technology, Russia) presented joint work with the University of Eastern Finland on 'The Synthesis of Catalytic Systems Based on Nanocomposites Containing Palladium and Hydroxycarbonates of Rare-Earth Elements'. For this work yttrium and cerium hydroxycarbonates were used as the support and Pd nanoparticles were directly reduced from solution. Nanocomposites $Pd/Y(OH)CO_3$ and $Pd/Ce(OH)CO_3$ were synthesised using two methods: (a) simultaneous production of a nanoscale substrate and immobilisation of Pd nanoparticles on its surface; or (b) prior synthesis of polyvinylpyrrolidone stabilised Pd nanoparticles followed by their immobilisation on the nanosized substrate surface. The new systems synthesised demonstrated high conversion efficiency and can be used for homogeneous catalyst production.

Applications of the Platinum Group Metals

Professor Zhuangqi Hu (Institute of Metal Research of the Chinese Academy of Sciences, Shenyang, China) explained the role of Ru in nickel-based single crystal superalloys. Over the last few years there has been increasing research on superalloy materials due to their high mechanical strength and oxidation resistance at elevated temperatures. Ni-based superalloys are widely used in turbine blades found in jet engines, ships and power plants. The blades operate in the hottest part of the engine at temperatures around 1100°C. The most recently discovered microstructure of superalloys is the third generation single crystal. By adding a refractory element, such as rhenium, strength is enhanced. However, over addition or segregation of Re causes topologically close packed (tcp) phase precipitation which damages the continuity of the microstructure, promotes crack initiation and leads to a decrease in strength of the superalloy. To prevent this, tests were made with Ru-free alloy and with alloys containing 1.5% and 3% Ru additions. Cast microstructure, structural evolution, tensility and rupture properties and oxidation behaviour were studied. It was noted that the addition of Ru suppressed tcp phase formation and hence improved the creep properties, so that Ru-containing superalloys could be used even under higher temperature conditions. There

was a strengthening effect on tensility, but no obvious effect on stress rupture life, and a weakening effect on heat/corrosion resistance. A higher oxidation rate was also observed when the Ru-containing superalloys were heated to 1000ºC or 1100ºC. The conclusion was that in future Ru might play an important commercial role in such superalloys.

Professor Yizhou Zhou (Institute of Metals Research of the Chinese Academy of Sciences, Xi'an, China) presented a paper entitled 'Effects of Platinum on the Micro-Segregation Behaviour and Phase Stability in Nickel-Base Single Crystal Superalloys'. In addition to the work on Ru discussed above, Pt has also been examined as a potential alloying addition to a third generation single crystal superalloy. However, experimental work on such materials has shown that the incipient melting point, solidus and liquidus temperatures are decreased. Pt segregates to the interdendritic region and intensifies the segregation of refractory elements such as Re and tungsten. Formation of a tcp phase is also promoted under extended thermal exposure at 1100ºC. Although Pt additions enhance tensile strength at high temperature, it is unable to enhance rupture life. It was concluded that Pt additions to single crystal superalloys do not have a beneficial effect on phase stability.

Professor Guang Ma (Northwest Institute for Non-Ferrous Metal Research, China) spoke on the topic of Pd alloy membranes in hydrogen energy. Hydrogen is an alternative energy source which could reduce our dependence on fossil fuels in the future. For many commercial applications hydrogen must be purified and the use of Pd-based alloy membranes for purification is very attractive. Pd-rare earth alloys have improved hydrogen permeability compared to other alloys used for this purpose (1). This is because the rare earth elements not only expand the Pd lattice but also readily adsorb hydrogen onto the membrane surface. Hydrogen separation rates increase with hydrogen permeability of the membrane. Improved mechanical strength, heat resistance and hydrogen diffusion rates, as well as the development of low cost manufacturing routes, are seen as important research and development targets for Pd-based hydrogen separation membranes.

Wei Li (General Motors, USA) reported on such issues as catalyst deactivation due to pgm sintering and poisoning, recent trends in the use of pgms in diesel catalysts (in particular the diesel oxidation catalyst (DOC), lean NOx trap (LNT) and diesel particulate filter (DPF)), different factors affecting catalyst performance, and the impact of future global emissions regulations on pgm usage in automotive emissions control catalysts.

Junjun He (Sino-Platinum Metals Co Ltd, China) presented a review of the metal–support interaction in automotive catalysts. The support can improve the dispersion of Pt, Pd and Rh and suppress the sintering of the pgms at high temperatures. The pgms can also enhance the redox performance and oxygen storage capacity of the support. The presentation reviewed the reaction phenomena and mechanism of pgms and supports such as Al_2O_3 and CeO_2-based composite oxides.

Vitaly Parunov (Moscow State University of Medicine and Dentistry, Russia) made a report on the biocompatibility of different denture materials based on research carried out amongst 109 patients. The noble metal-based alloys Plagodent and Palladent (fabricated by Supermetal, Russia) showed the best results when compared to other types of metal-based materials.

PGM Refining Technologies

Joseph L. Thomas (Metals Recovery Technology Inc (MRTI), USA) explained MRTI's commercial precious metal recovery technologies. Recently, four different types of pgm-containing waste feedstock have been treated:

(a) Pd was recovered from various supported Pd catalysts (100–5000 ppm Pd) by chlorine leaching. After addition of chlorine and polyamine resin, a Pd-loaded polyamine composite resin (2) was produced, while other metals (e.g. Ni, copper and iron) remained in solution. The capacity was 20 Mt per batch with a five day cycle and a recovery rate of 99% Pd.

(b) Pt, Pd or gold were recovered from Cu alloys containing these metals. After adding Cu metal to Pt, Pd or Au ores or spent catalysts, the mixture was melted by induction to give the Cu alloy. Then sodium chloride and chlorine gas were added. The dissolved precious metals were then reduced to insoluble solids and separated from the solution.

(c) Pd, Pt, rhodium and Au were recovered from spent autocatalysts. The reaction again involved the addition of chlorine together with resin to the autocatalysts. Only Pd, Pt, Rh and Au were absorbed onto the resin while other metals, including Group I and Group II chalcogens and other transition metals, were not. The metal resins were then burned to yield metal of 98–99% purity.

(d) The pgms were recovered from a complex mixture of pgms and other transition metals. The pgms were refined using a substituted quaternary ammonium salt (2) giving more than 99.9% pgm recovery with a typical purity of 99.97% to 99.99% in six days. The procedure relied on precipitation, filtration and washing and did not involve ion exchange or solvent extraction. This is based on the fact that only pgms will precipitate with tetramethylammonium chloride. The reagent may be recycled after use.

Professor Jinhui Peng (Kunming University of Science and Technology, China) reviewed the recovery of pgms from secondary resources using microwave technology. This is believed to be more efficient, energy-saving and environmentally friendly than conventional metallurgical process. Three different approaches were discussed:

(a) Microwave-assisted leaching improved the yield and process time for the recovery of pgms from spent catalysts. After microwave heating at 600ºC for 60 minutes, the leaching efficiencies of Pd and Rh were 99.8% and 97.4%, respectively (3).
(b) Microwave pyrolysis was used to recycle pgms from waste printed circuit boards. The waste circuit boards were initially crushed into small pieces and microwave heated to decompose organic compounds. Subsequent heating to 1100ºC allowed the pgms to be separated and recovered.
(c) Microwave augmented ashing was used to reduce the length of time required for the activation process for recovery of Pt and Rh from scrap firebricks from the glass industry.

Although microwave assisted pgm recovery was still at the laboratory stage, it has potential to be a next generation pgm refining technology due to its environmental benefits.

Market Trends and the PGM Industry

Mikhail Piskulov (Johnson Matthey Moscow, Russia) reported on recent trends in industrial pgm applications. It was noted that industrial applications play an important role in the pgm markets, accounting for 25–30% of the gross total demand for Pt and Pd and close to 100% for such minor pgms as Ru and Ir. In the last 10 years industrial demand has been on the increase over the entire pgm range. However, there is a constant need for new research and development to fully explore and develop new areas which can benefit from the unique properties of pgms.

Alexander Andreev (Ekaterinburg Non-Ferrous Metals Processing Plant, Russia) outlined in his paper the role of Russia in the global pgm markets and the problems faced by Russian exporters due to internal regulations. Andreev estimates that in 2011, the Russian share of global pgm supply amounted to 13% (26 tonnes) Pt, 47% (108 tonnes) Pd and 8.9% (2.12 tonnes) Rh. However, the Russian share of world pgm trade was much lower. The discrepancy was explained by a lack of metal trading activities in Russia, compared to the European and Asian markets, largely due to concentration of demand (end users for sectors like electronics and automotive) in these regions, but also due to issues related to the limitations and shortcomings of Russian customs and currency regulations.

Mariya Goltsova (Donetsk National Technical University, Ukraine) presented the 'Hydrogen Civilization (HyCi) Doctrine', which describes a vision of sustainable development, starting with a gradual change to the use of hydrogen energy, followed by a more integrated hydrogen economy and finally what the HyCi doctrine calls a 'hydrogen civilisation'. The authors anticipate that this will lead to global transformation in all aspects of life, society, the environment and industrial development.

Jurgen Leyrer (Umicore AG & Co, Belgium) outlined Umicore's 'Process Exellence Model' for the special glass and chemical industries. Umicore defines process excellence as any achievement related to Pt components before, during or after use in a customer's production process. They claim to offer cost savings, for example by reductions in pgm inventory and pgm losses in operation and during refining, reduction of Rh requirements, energy and raw materials and increase in the service time of pgm components.

Liudmila Morozova (Supermetal) made a presentation on this Russian fabricator's pgm product manufacturing activities. The company has been active for 50 years, and for the last 25 years it has been fabricating equipment for the production of high-quality glass and monocrystals as well as other pgm products for technical and medical applications. They use pyrometallurgical processing of scrap with high pgm content, which allows scrap alloys to be refined without dealloying, substantially accelerating processing time and reducing costs. They also use electrophysical fabrication technologies to produce dispersion strengthened materials (DSMs) based

on Pt and its alloys with Rh. DSMs allow the use of manufacturing techniques such as rolling, stamping, drawing and welding, while the heat resistance of DSMs (as measured by the creep rate and long-term strength under operational temperatures and stresses) is tens of times higher than that of traditional Pt-Rh alloys. Laminar composite materials (LCM) combine the properties of regular Pt-Rh alloys with the improved heat resistance and thermal stability of DSMs. In combination with a new technology for producing solid stamped bushing base plates, bushings can be made 20–30% lighter with increased service life. The company also manufactures thermocouple wire and catalyst systems and catchment packs for the nitric acid industry.

Pavel Khorikov (Krasnoyarsk Non-Ferrous Metals Plant, Russia) reported on the company's fabrication of bushings and other glass making manufacturing units. The current bushing production range is 200–4000 tips. Materials include dispersion stabilised Pt10Rh DS. They also make combination bushings, where a bushing body manufactured from Pt20Rh alloy is welded to a base plate of Pt10Rh DS. In the first five months of 2012 the total weight of fabricated pgm products for the glass industry made by the company was in excess of 160 kg.

Conclusions

A number of pgm topics were covered during this conference including pgm nanostructures, superalloys, pgm refining, dental materials, emissions control and fabricated products, as well as market based information. In 2012 China was the world's leading platinum consuming country (4), and Kunming PM'2012 was a good platform for rest of the world to understand the most recent pgm developments in China and elsewhere. The conference was followed by a visit to Kunming Institute of Precious Metals and Sino-Platinum Metals Co, Ltd. The Kunming Institute of Precious Metals has published the "Precious Metals Blue Book" and distributed hard copies during the conference. A total of 63 papers were published in English and the conference proceedings are available (5).

The next conference in this series will be held in 2014, venue to be decided upon.

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The Reviewers

Dr Mikhail Piskulov is General Manager of Johnson Matthey Moscow, Russia, where he is involved in market analysis, sales and new business development. Dr Piskulov graduated from Moscow State University of International Relations with a degree in International Business. Before joining Johnson Matthey in 1993, he worked for the USSR Ministry of Foreign Trade. He holds a PhD in Economics, obtained in 2002, on the competitive advantages of foreign direct investment for the receiving country.

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"Precious Metals Blue Book"
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