International Conference on "Noble and Rare Metals"

METALLURGICAL AND MINERALOGICAL STUDIES OF THE PLATINUM GROUP ELEMENTS AND COMPOUNDS IN THE CIS

Academic, technological and economic aspects of platinum group elements were quite comprehensively included in the programme of the NRM-94 (Noble and Rare Metals) conference held from 19th to 22nd September 1994 in the State University of Donetsk, Ukraine, under the Chairmanship of Professor V. A. Goltsov. Contributions to the programme were divided into three main sections, each comprising some forty oral and forty poster items. Significant numbers of reports within each section emphasised the depth of resources and breadth of investigations involving platinum metals by scientists from the Commonwealth of Independent States, with most of the papers originating from Russia and Ukraine. There were 296 participants, mostly from Ukraine and Russia; other attendees came from Uzbekistan, Belorussia and Khazakhstan, Great Britain, Germany, Japan, and the U.S.A. These participants represented various research institutes, universities, industrial firms and government bodies.

Mineralogical and Other Platinum Metals Sources and Their Recovery

Section 1 of the Conference was centrally concerned with sources of mineral concentrations and the abstraction and recovery of the platinum group metals. With regard to mineralogical sources, a general survey and overall assessment of the mineral wealth of Ukraine was presented by B. S. Panov, (State Technological Institute, Donetsk). Contributions more specifically dealing with the isolation of the platinum metals from non-traditional shales, and from wider deposits in the Aldan Shield area, were presented, respectively, by A. F. Korobeinikov and colleagues (Polytechnic Institute, Tomsk, Russia) and V. V. Stogny and colleagues (State University, Yakutsk, Russia); and isolation from waste deposits in the Don Basin coal mines was discussed by A. F. Gorovoi and colleagues, (Mining and Metallurgical Institute, Alchevsk, Ukraine).

Papers concerned with the abstraction of platinum metals from various industrial wastes included one discussing the treatment of Chineisk dissolved wastes (B. I. Gongal'sky and colleagues, Institute of Natural Resources, Chita, Russia); while the abstraction of platinum metals from general and from secondary scrap was discussed, respectively, by A. A. Mazhan and colleagues (State Alloy Institute, Donetsk) and S. I. Pechenyuck and colleagues (Institute of Chemistry and Technology of Rare Metals and Minerals, Apatity, Russia). Techniques of abstracting platinum metals from sulphuric acid solutions with thiourea derivatives were described by Yu. A. Mirgorod (State Institute, Sumy, Ukraine) and ways of separating platinum metals from nuclear fuel wastes were described in papers by Yu. A. Sidorenko and colleagues (Alloy Company, Krasnoyarsk, Russia), V. I. Volk and colleagues, and E. V. Renard (all of the A. A. Bochvar Institute of Inorganic Materials, Moscow).

Platinum Metals Chemistry and Electrochemistry

Various aspects of the general and complex chemistry of platinum metals were discussed in Section 2 of the Conference, including: the redox properties of 4-valent rhodium, by A. V. Khaperskaya and colleagues (All-Russia Science Research Institute, Moscow); properties of rhodium and platinum complex compounds with phosphorus and silicon, by V. N. Nazmutdinova and colleagues (Institute for General and Physical Chemistry, Kazan, Russia); and studies of the phosphides of platinum, by V. B. Chernogorenko and colleagues (Institute for Problems of Materials Science, Kiev). Studies of ruthenium and osmium complexes were reported by O. Ya. Borovaya and colleagues (Lvov Polytechnic Institute, Ukraine).

Several presentations were concerned with the precipitation, deposition and other electrochemical problems of the platinum group metals; these included studies of anodic processes on platinum anodes by N. M. Barbin (Institute of High Temperature Electrochemistry, Ekaterinburg, Russia); and the electrochemical behaviour of palladium ions in a melted eutectic mixture of sodium and caesium chlorides, by N. P. Borodina and colleagues (also from the Institute of High Temperature Electrochemistry). The electrodeposition of iridium was discussed by N. V. Grushina and colleagues (Institute of Organic Chemistry, Catalysis and Electrochemistry, Almaty, Khazakhstan); and new methods for refining iridium were described by A. A. Omel'chuck (Institute of General and Inorganic Chemistry, Kiev). The mechanical behaviour of iridium and ruthenium was described by P. E. Panfilov and colleagues (Ural State University, Ekaterinburg) and osmium extractions from sulphuric acid solutions was discussed by I. D. Troshkina and colleagues (Russian Chemical and Technological Institute, Moscow).

Other topics discussed were palladium alloy electrodeposition and utilisation by S. N. Vinogradov and colleague (State Technical University of Penza, Russia); electrodeposition of palladium based alloys in preference to palladium and gold by T. V. Slyusarskaya and colleagues (State Educational Institute, Kharkov, Ukraine); and rhodium plating by electrodeposition by A. V. Boiko and colleagues (also from the State Educational Institute).

Techniques of Platinum Metal Analysis

A contribution from M. K. Nauryzbaev and colleagues (State National Institute, Almaty) on methods for the determination of palladium in alloys and catalysts, presented a general review of available techniques. In analytical papers, centred on more specific methods, A. A. Valter and colleagues (Institute of Geochemistry, Mineralogy and Ore Production, Kiev, Institute of Applied Physics, Sumy, and Physico-Chemical Institute, Kharkov), reported on nuclear physical methods for noble metal analysis; Kh. Kh. Turaev (State Institute of Termez, Uzbekistan) reported on the radiometric determination of palladium and N. A. Kolpakova and colleagues (Polytechnic Institute, Tomsk) reported on the inversion voltammetric determination of platinum metal composition. Two papers concerned with analysis of platinum metals sorbed on porous media were introduced by A. S. Karasick and colleagues (Engineering and Technological Centre of Powder Metallurgy, Perm, Russia) and I. P. Bakhvalova and colleagues (Research Engineering Centre, Krasnoyarsk). S. I. Degtyarev and colleagues (State University, Yakutsk) reported on γ-ray methods for the analysis of noble metals.

Physical and Technological Aspects of Platinum Metals and Alloys

Contributions which concentrated mainly on physical and technological aspects were the basis of Section 3 of the conference programme. Production of palladium powders was discussed in a paper by D. R. Shul'gin and colleagues (Institute for Non-Ferrous Metals, Krasnoyarsk) and the production and use of articles of noble metal alloys was reviewed by D. S. Tykochinsky (Scientific Production Complex, "Supermetal", Moscow). The advantages of reduced corrosion of platinum metals in molten oxides was reported on by V. P. Kochergin and colleagues (Ural State University, Ekaterinburg); while the loss of platinum metals from catalysts employed in nitric acid production was discussed by A. Yu. Chernyshev and colleagues (State Institute of Nitrogen Industry, Moscow) and the regeneration of catalysts based on platinum alloys was the subject of a contribution from A. S. Savenkov and colleagues (Polytechnic Institute, Kharkov). The influence of the platinum metals on martensite transformations was discussed by E. L. Semenova and colleagues (Institute for Problems of Materials Science, Kiev) and a review on the casting of noble metals and noble metal alloys was presented by S. P. Doroshenko (Polytechnic Institute, Kiev).

An account of phase transitions in palladiumrich palladium-rare earth alloys was presented by Y. Sakamoto (University of Nagasaki, Japan) and an account of interdiffusion in the gold-platinum system was given by M. Onishi and colleagues (Kyushu Institute of Technology, Japan). Two papers about the palladium-gold-iron system alloys were presented by authors from the Ural State Technical Institute, Ekaterinburg; one, by Yu. K. Serdyuk and colleagues, covered the influence of ordering on physical properties, while the other, by I. I. Piratinskaya and colleagues, was on the effect of melt heat treatment on magnetic state.

Stepwise ordering in alloys of iron-palladium-gold was discussed by S. Yu. Zaginaichenko and colleagues (Metallurgical Institute, Dnepropetrovsk, Ukraine) and a study by computer engineering of equilibria in ternary alloy systems was reviewed by O. M. Irbeltkhaeva and colleagues (Buryat Institute of Natural Science, Ulan-Ude, Russia). A review of the scandium-ruthenium system was presented by V. G. Khoruzhaya and colleagues (Institute for Problems of Materials Science, Kiev).

Studies with electronic and biological interest were presented in papers concerning radio modifiers based on palladium alloys by I. A. Efimenko and colleagues (Kurnakov Institute of General and Inorganic Chemistry, Moscow), and in papers which discussed the uses of platinum compounds in chemotherapy. These included platinum complexes which display anti-tumour properties, discussed by A. L. Konovalova and colleagues (Oncology Science Centre, Moscow and Chemico-Pharmaceutical Institute, St Petersburg); and acetylene complexes of platinum potentially exhibiting biological activity presented by L. L. Sichinava and colleagues from the V. I. Nikitin Institute of Chemistry, Dushanbe, Tadzhikistan.

Hydrides: Hydrogen Permeation Membranes

The research involvement of Professor Goltsov's Donetsk group in studies of hydrogen in metals has been emphasised by the regular appearances of their extensive Russian-English translations database in the *International Journal of Hydrogen Energy*. The database is a compilation of Russian hydrogen energy and metal-hydrogen publications. This high level of involvement was reflected at the conference by the inclusion of a special section on contributions involved with metal/hydrogen interactions, most importantly concentrated on aspects of the palladium-hydrogen and allied systems. In this section a general review of phase relationships and thermodynamic aspects of metal-hydrogen systems, with emphasis on statistical thermodynamic correlations, was presented by H. Brodowsky and colleagues (University of Kiel, Germany and the University of Sendai, Japan). Further information concerning the phase relationships and related structures of palladium-rare earth alloy-hydrogen systems was presented in relation to recent extensive series of allied contributions in this field of study, by Y. Sakamoto and colleagues (University of Nagasaki).

Two papers, containing information of further research into possibilities of technologically attractive evidence of cold fusion in hydrogen isotopes discharged electrolytically at palladium surfaces, but with different perspectives and representations of experimental results, were contributed by J. S. Cantrell (Miami University, Ohio, U.S.A.) and T. Matsumoto (Hokkaido University, Sapporo, Japan). Interrelationships between lattice hardening and strengthening effects of interstitial hydrogen in relation to phase (p-c(n)-T) relationships in the palladium-hydrogen system, were subjects of a wide ranging review of progress in regard to these factors by Professor Goltsov.

This review served as a background for several related oral and poster presentations by members of the Donetsk group, including contributions by R. V. Kotelva and Goltsov, and by Yu. A. Artemenko and M. V. Goltsova. An important concern with the use of palladium alloys as hydrogen permeation membranes, was the basis of a contribution presented by Goltsov, A. P. Kuzin and colleagues.

Hydrogen permeation through palladium alloy membranes was also a central topic of contributions from other centres with allied interests.

Thus the influences of palladium membrane coating on hydrogen permeation through iron were discussed by Y. Hayashi and colleagues (University of Fukuoka, Japan) and comparisons of hydrogen permeabilities in palladium-yttrium(gadolinium)-silver and palladium-yttrium-indium(tin, lead) alloys were reported by Y. Sakamoto and colleagues (University of Nagasaki). Evidence from observations of 'uphill' hydrogen permeation effects, originating from self induced strain gradients, and consequent Gorsky effect hydrogen migration, that result from the lattice expansive nature of hydrogen interstitials, was reviewed by F. A. Lewis (University of Belfast). A survey of potential applications and general prospects for the development of palladium alloy membranes for hydrogen purification and catalytic utilisation was presented by V. G. Sorokin ("Lenneftekhim", St Petersburg), and the application of mathematical modelling to clarify the process mechanisms of hydrogen permeation in palladium alloys was outlined by A. M. Dobrotvorsky and colleagues (also of "Lenneftekhim"). A broader general assessment of the prospects for utilising palladium and palladium alloys in future hydrogen research was presented by P. G. Berezhko (Scientific Research Institute of Experimental Physics, Arzamas, Russia).

Substantial details of the contents of the papers were available in books of abstracts, most of which were in Russian, the remainder being in English. The location of the next conference in this series has yet to be finalised, and enquiries should be addressed to Professor V. A. Goltsov in Donetsk. F.A.L.

A Copper-Free Ruthenium Perovskite Superconductor

In recent years layered perovskite structures exhibiting superconductivity at low temperatures have been synthesised. Work on these compositions, with various substitutions, has resulted in materials which display significantly higher transition temperatures, and hence are superconducting at relatively higher temperatures. These increases in transition temperature are sufficiently large to suggest that a market for such materials is likely to develop during the last few years of this century.

Materials developed to-date are based upon systems, such as $La_{2-x}Ba_xCuO_4$, where the copper is present in layers, together with oxygen. This layering is necessary to induce superconductivity, as are the barium substitutions into the basic perovskite structure. However, work is now reported on the evaluation of a perovskite compound based on $Sr_{n+1}Ru_nO_{3n+1}$ (Y. Maeno, H. Hashimoto, K. Yoshida, S. Nishizaki, T. Fujita, J. G. Bednorz and F. Lichtenberg, *Nature*, 1994, **372**, (6506), 532–534). When $n=1$ Sr_2RuO_4 is formed, having crystal structure isostructural with $La_{2-x}Ba_xCuO_4$.

Single crystals of Sr_2RuO_4 were cleaved, and measurements made which revealed superconductivity below about 1 K. The transition temperature, T_c, was 0.93 ± 0.03 K. Critical current density measurements were made at 0.32 K.

While Sr_2RuO_4 does not possess the higher transition temperatures likely to be the basis for future opportunities, the system may be important for a basic understanding of such materials, since comparison with other superconductors with significantly different T_c values will help to explain the role of the various electronic components of the superconducting effect.

In conclusion it should be noted that this work demonstrates that the presence of copper is not a prerequisite for the existence of superconductivity in layered perovskites, but that the high transition temperatures possible when it is present would appear to indicate that it has a special role. On this basis the existence of superconductivity in Sr_2RuO_4 may be a valuable discovery, particularly to clarify the mechanisms permitting superconductivity. A.S.P.

A Palladium Source of Protons

The use of very bright gaseous sources for lithographic purposes has been suggested, but no practical ion sources have been found.

Now, however, researchers from the Muroran Institute of Technology in Japan, have made a preliminary proton ion source using palladium (T. Teraoka, H. Nakane and H. Adachi, *Jpn. J. Appl. Phys., Part 2 Lett.*, 1994, **33**, (8A), L1110–L1112), making use of the fact that palladium has the highest hydrogen permeability of all metals. The needle-shaped palladium allows hydrogen diffusion at the same rate as it permeates in bulk palladium. The ion source must be operated so as to avoid a phase transition which occurs at 100–200°C in the palladium. The ion source is expected to be useful for future microfabrication technology.