

Platinum Metals Catalytic Systems in Nitric Acid Production

SYSTEM OPTIMISATION IN NON-CONCENTRATED ACID PLANTS

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The State Institute for the Nitrogen Industry is one of the oldest industrial branches of the research and engineering institutes in Russia and the former U.S.S.R., and in 1991 the Institute celebrated its sixtieth anniversary. This paper gives a brief overview of the main results of work carried out by GIAP alone and in co-operation with other organisations over the past 50 years on the optimisation of the production of non-concentrated nitric acid. In particular developments to reduce the amounts of platinum group metals used in ammonia oxidation and waste gas cleaning, and ways to reduce platinum group metal losses are discussed.

At present the states of the former U.S.S.R. (CIS) produce about half of the total world output of non-concentrated nitric acid, and have in use at all times approximately 6 tonnes of platinum-rhodium-palladium alloys as catalysts for the conversion of ammonia to nitrous oxide, and about 8 tonnes of palladium in catalysts for the removal of residual nitrogen oxide from the waste gas. Annually the non-recoverable loss of platinum-rhodium-palladium alloys amounts to over 1 tonne. Nitric acid plants use the greatest quantities of the platinum group metals of all the plants developed and engineered by GIAP. All these nitric acid plants developed by GIAP utilise equipment manufactured by Russian and Ukrainian enterprises. Over 70 per cent of the total nitric acid output is produced by modern large scale UKL-7 and AK-72 type plants, which produce 355 and 1150 tonnes of nitric acid/day, respectively. The temperatures of the catalytic gauzes in the ammonia oxidation reactors in UKL-7 and AK-72 units are 900 and 840°C, respectively, and the pressures are 0.7 and 0.4 MPa, respectively (1). In this process, the ammonia conversion stage critically determines the specific consumption of both ammonia and of the platinum-rhodium-palladium catalyst per tonne of the final product. The approximate

metal losses per tonne of acid produced in UKL-7 and AK-72 are 0.135 and 0.12 g, respectively. About 85 per cent of the manufacturing cost of nitric acid comes from the cost of the ammonia and the platinum metals catalysts.

This paper reviews briefly the main results of work on the optimisation of platinum group metals based catalytic systems for the production of non-concentrated nitric acid. It should be noted that the technical approaches reported below for ammonia conversion can also be used to advantage for the manufacture of hydroxylamine sulphate, prussic acid and other chemical processes which have a catalytic ammonia processing stage as part of their production.

Ammonia Conversion Stage

The first development by GIAP in the field of ammonia oxidation catalysts dates back to World War II, and was caused by an acute shortage of rhodium in the U.S.S.R. As a result, an alloy catalyst was developed which comprised 92.5 per cent platinum, 4 per cent palladium and 3.5 per cent rhodium (2). The catalyst was designated GIAP-1. Experience gained over many years has shown that the GIAP-1 catalyst is as good as its prototype—the platinum-rhodium alloy containing 92.5–93 per cent platinum and

7–7.5 per cent rhodium, patented by Du Pont. By 1949 all the nitric acid plants in the U.S.S.R. were using the domestic GIAP-1 catalyst. With the present day cost of rhodium being significantly greater than that of platinum, and especially that of palladium, this development remains topical.

The successful attempt to replace part of the rhodium by palladium in the Du Pont catalyst formulation encouraged the research workers at GIAP to continue their intensive investigations in this direction. However, it took another 25 years of painstaking research before the next major advance produced a new catalyst containing lower rhodium and platinum contents (3, 4). This catalyst with the trademark GIAP-5 contains 81 platinum-15 palladium-3.5 rhodium-0.5 per cent ruthenium. Compared to the GIAP-1 alloy, it has a higher resistance to catalytic poisons and a 20 to 25 per cent higher mechanical strength, giving reductions in both the amount of platinum group metals and their loss during the ammonia oxidation stage of 7–9 and 15–25 per cent, respectively.

In the early 1970s the U.S.S.R. began a programme to change over from the GIAP-1 catalyst to the GIAP-5 catalyst in nitric acid plants. The programme was completed in 1975. Throughout that time there was much controversy between plant managers and research workers of various organisations about the advantages and disadvantages of both alloys. Opponents, although acknowledging the above mentioned advantages of GIAP-5, claimed that there were cases when it showed a lower ammonia to nitric oxide conversion rate than the GIAP-1 alloy. This was principally due to the fact that at the time GIAP did not have a satisfactory physico-chemical procedure to determine the ammonia to nitric oxide conversion rate (this procedure will be discussed below). The controversy was largely resolved by a special purpose study carried out in 1977 by GIAP in co-operation with the Institute for Chemical Physics, Chernogolovka, Russian Academy of Sciences (ICPCh RASc) (5). During this study the ICPCh RASc used a unique high-precision electrothermographic method to measure the dynamic characteristics

(activity, reaction wave propagation velocity, surface macrorelief reconstruction rate, etc.) of both catalysts and of pure platinum in the ammonia oxidation reaction conducted in a laboratory environment. In addition, commercial testing was carried out for two comparable gauze packs of both alloys installed in two parallel ammonia oxidation reactors of diameter 4 m at the AK-72 plant, at the Kirovo-Chepetsk Chemical Works, each reactor having seven catalytic gauzes. The total weights of the packs of gauzes for GIAP-1 and GIAP-5 are approximately 77 and 73.5 kg, respectively. As a result, it was found that the GIAP-5 catalyst provided a yield of the target nitric oxide product which was approximately 1.5 per cent lower than the GIAP-1 alloy, for an ammonia/air mixture reasonably free of chemical poisons and mechanical impurities. However, the findings of that study (5) still did not satisfy some investigators and caused new discussions, reported in further papers (6, 7).

Therefore in 1991, because of continuing interest in partially replacing platinum by palladium in the ammonia oxidation catalyst, it was thought necessary to carry out another commercial test to examine the economic advantage. For this purpose, two comparable packs each containing seven catalyst gauzes were installed in two parallel reactors at the AK-72 plant operated by the Dorogobuzh Minudobreniya (Fertiliser) Industrial Association. The first pack consisted of GIAP-5 alloy gauzes and the second one comprised Du Pont alloy gauzes. Using GIAP's optimised procedure (see below) measurements of the ammonia to nitric oxide conversion rate (the β -factor) were taken throughout the specified operating life of the catalysts, which is six months in a AK-72 plant. The ammonia load on each of the two parallel reactors of the AK-72 unit is up to 10,000 nm^3 per hour. During the first two months the β -factor for the Du Pont alloy was approximately 1.5 per cent higher than that of the GIAP-5 alloy. However, after that the two β -factors became equal, and in the final third of the operating period the β -factor for GIAP-5 exceeded the β -factor for Du Pont by approximately 1.5 per cent. Arithmetic mean values of the β -factors for both alloys were virtually equal

over the period under study. Analysis has shown that this pattern of time dependence for the β -factors is due to the fact that the GIAP-5 catalyst has a higher resistance to chemical poisons present in both the air and the ammonia. Thus, when selecting an ammonia conversion catalyst, it is necessary to consider the purity of the air and ammonia at the specific plant site. It is generally known that in most nitric acid plants the air and especially the synthetic ammonia, used as the feed gases, contain a considerable amount of chemical impurities that are poisonous to the catalyst. Despite this most of the present day nitric acid plants worldwide are fitted with filters that only remove particulate impurities and oil from the air and ammonia feed gases.

Careful analysis of the results of these field trials was performed using the technique developed by GIAP for calculating the process of ammonia oxidation "from gauze to gauze". This led to the conclusion that it was possible to reduce the total number of gauzes in a pack without incurring a corresponding loss in the nitric oxide yield, if gauzes made from alloys of differing platinum content were arranged in an appropriate order within the pack. As a result in 1987 GIAP, in co-operation with ICPCh RASc, developed catalyst packs containing a unique combination of gauzes made from high (> 92.5 per cent) and low (\geq 81 per cent) platinum content alloys. These provide savings in the amount of platinum group metals used and lost of approximately 14 and 10 per cents, respectively. This engineering design has been used to advantage in a number of Russian AK-72 plants for over 5 years.

GIAP has more than 25 years of pioneering experience in the development and commercial operation of a number of modified two-stage ammonia oxidation processes using part of a pack of standard platinum gauzes and a bed of non-platinum oxide catalyst granules acting as the first and second stage catalysts, respectively. These systems reduce the mass of used platinum group metals by 40 to 66 per cent and irrecoverable loss by 25 to 30 per cent. The most generally used non-platinum catalysts are based on iron oxides and designated KH-2, HK-2Y and KH-CX2 (8-10). These are available as $5 \times 5 \text{ mm}^2$

pellets of bulk weight 1300 to 1700 kg/m^3 , with a service life of four to seven years. Careful analysis of data from the commercial operation of these systems over the past decade shows that they can be used without a drop in nitric oxide yield only if the proportion of ammonia processed at the second stage is fixed. (The value of this proportion and the formulation of the non-platinum catalysts are not divulged by the developer.) More stringent requirements in reactor design and operating procedures are of vital importance when using this type of system. The reactor design should include a uniform non-platinum catalyst bed of about 100 mm thickness. The reactor must be equipped with a system to prevent the reverse flow of gas through the catalytic element. All atmospheric pressure reactors operated in the CIS are equipped with similar catalytic systems. About 30 per cent of the nitric acid output per year in the CIS is produced in 200 atmospheric pressure units, each unit having two parallel oxidation reactors of 3 m diameter. Recently such systems have been delivered on contract to Syria and Romania.

It is believed that these catalytic systems can be developed further by creating a non-platinum catalyst of regular honeycomb structure, which will give greater uniformity in the gas mixture flow field both upstream of the platinum gauze bed and in the first stage catalyst bed itself. This is expected to increase the activity and selectivity of the first catalytic stage and, hence, of the two-stage catalyst as a whole. At present GIAP has successfully completed pilot tests of such a catalyst in a reactor of diameter 0.22 m (11), and several prototypes have been made for test in UKL-7 plants in 1992-93. There is one oxidation reactor in the UKL-7 unit with a diameter of 1.65 m and according to the design the reactor is equipped with 12 GIAP-5 gauzes of approximately 24 kg total weight. The ammonia load of this reactor is up to 6000 nm^2 per hour.

Optimised Physicochemical Procedure

Around 1977 it was realised that further improvements in the ammonia oxidation catalytic systems would not be possible without first

improving the physicochemical procedure for determining the ammonia to nitric oxide conversion rate—the β -factor. Close analysis of all such procedures available worldwide, which we carried out by the error analysis method (12)*, has shown that they allow the β -factor to be determined with an aggregate absolute error of about ± 2.4 per cent at the confidence level of 0.95 (aggregate absolute error is known to include inherent systematic and random errors). With such inaccurate procedures it is impossible to judge rigorously the efficiency of a newly developed catalyst system which may have, for example, a 1.5 per cent higher or lower yield of nitric acid than the prior art system.

The physicochemical procedure was developed and standardised, to improve the assessment of the ammonia to nitric oxides conversion rate, and equipment was designed (13). This procedure has an aggregate absolute error of ± 0.75 per cent at the confidence level of 0.95. The procedure gives the added advantage that its error decreases \sqrt{n} times with the increasing number of parallel ammonia oxidation reactors in a nitric acid plant, where n is the number of parallel reactors. Using this procedure it was possible to improve and develop further the catalytic systems for ammonia oxidation and the procedure is currently used by a number of Russian enterprises.

In 1990–1992 it was delivered to Romania and Hungary as part of larger engineering contracts.

Mixer Designs for Uniform Flow and Concentration Fields

When a change over to large scale ammonia oxidation reactors, containing catalyst gauzes of over 3 m in diameter, was made it was necessary to ensure uniform flow and concentration fields in the ammonia/air mixture stream upstream of the catalyst bed. Investigations in the early 1980s had shown that the nitric oxide yield decreased by 1 to 1.5 per cent when the ammonia concentration and the average ammonia/air mixture velocity (measured at different points in the cross-section of the reactor upstream of the platinum

* For a number of purely technical reasons, the publication of the paper (12) was delayed until 1991

catalyst bed) departed from their average flow values by ± 7 and ± 30 per cent, respectively (14). These non-uniform parameters in commercial ammonia oxidation reactors were measured by the aerodynamic modelling method (15, 16).

Most of the currently used ammonia/air mixers cause non-uniformities in the concentration fields of about ± 4 per cent and, more importantly, give rise to an explosion hazard. GIAP was the first organisation in the world to develop the necessary and sufficient conditions for physically modelling all the operations of a commercial mixer based on a single structurally similar pilot unit (17, 18). Based on this model new designs for mixing ejectors have been developed, tested and successfully operated in a number of UKL-7 and AK-72 plants in Russia and abroad. These produce homogeneous mixing to at least ± 1.3 per cent and exclude the risk of explosion throughout their service life.

Aerodynamic modelling (15, 16) has also shown that space non-uniformities throughout the ammonia/air mixture flow field in commercial reactors over the platinum metals catalyst are ± 30 – 40 per cent of the average flow velocity and that the amplitude of the turbulent fluctuations in the ammonia/air mixture flow (time non-uniformities) are 50–60 per cent of average flow velocity at around 100 Hz. These non-uniformities reduce the nitric oxide yield from the reactor by about 1 to 2 per cent. In order to eliminate these non-uniformities new designs for deturbulating distributors have been developed (19) and successfully introduced in UKL-7 and AK-72 nitric acid plants, which have typical conversion efficiencies of 93.5 and 95 per cent, respectively, with GIAP-5, so increasing the nitric oxide yield by 1 to 2 per cent.

As a result of studies of the non-uniformity in the flow field, the gas passing through the platinum metals catalyst gauze bed was laminated. It is apparent that steady conditions in the gas dynamics over the catalyst bed can be achieved by gas dynamics screening the gauze packs and by using combined packs containing non-catalytic elements. This design has been developed in co-operation with ICPCh RASc. Here the

inventive steps are the materials and the structural assembly of the non-catalytic elements in the pack. It is known that if spaces exist between the platinum group metals gauzes in a catalyst pack the ammonia decomposes to nitrogen in the voids, which reduces the yield of nitric oxide (20).

Comparative field tests of the combined gauze pack and the pack of platinum group metals gauzes, carried out in parallel ammonia oxidation reactors in the AK-72 plant at the Kirovo-Chepetsk Chemical Works, have shown that the combined packs reduce the loss in the platinum group metals by 1.4 to 1.6-fold, while ensuring the same ammonia conversion rate.

Another way to ensure steady gas dynamic conditions over the gauze bed is to laminate the flow of nitrous gases downstream from the gauze bed (21). This is achieved by installing a unique device having a regular arrangement of baffle plates to divide the flow of nitrous gases into a host of parallel jets, downstream of the gauze pack (22). Tests performed on the baffle pack in UKL-7 plants, belonging to the Cherkassy Azot (Nitrogen) Industrial Association (IA), the Rovno Azot IA and the Dorogobuzh Minudobreniya (Fertiliser) IA, have shown that it reduces platinum group metals loss by at least 15 per cent. In the absence of other gas flow distribution devices, it increases the nitric oxide yield by 1 to 1.5 per cent.

In 1971 GIAP embarked on an extensive project for recovering platinum group metals immediately downstream from the gauze bed. At that time the use of palladium-gold alloy catchment gauzes for trapping platinum group metals, which had been developed by Degussa, was well known (23). However, the economic situation in the U.S.S.R. at that time was such that it was not possible for a catchment gauze to be fabricated containing a noble metal sorbent. Therefore GIAP, together with the Kharkov Polytechnic Institute, set out to develop sorbents based on calcium oxide. After overcoming many difficulties resulting from inadequate strength, inefficiency, high hygroscopicity, etc. (9) several types of granular sorbent based on aluminium and calcium oxides were developed (24). The sorbent

bulk weight is 1050 kg/m³, the height of the bed in the reactor is 150 to 200 mm and its gas dynamic resistance is 500 to 1000 Pa. The platinum group metal recovery rate is about 50 per cent of direct loss. The sorbent collects both the volatilised platinum and the particulates and it has been successfully used in a number of AK-72 plants.

Further/Future Developments

For the future one of our latest developments achieved in co-operation with the Instytut Nawozow Sztucznych (Pulawy, Poland) may hold most promise. This is a catalytic system comprising platinum-rhodium gauzes, palladium alloy gauzes and a bed of the above described sorbent (25). An important feature is that the palladium alloy gauzes serve as both catalyst and catchment gauzes (26). Compared to a conventional pack comprised of only platinum-rhodium gauzes, this system achieves a 33 to 50 per cent lower platinum group metals mass and the irrecoverable platinum loss is reduced by a factor of 10 or more. Commercial testing of this system began in March 1993 at the AK-72 plant of the Dorogobuzh Minudobreniya (Fertiliser) IA.

The start-up operation for the ammonia oxidation reactor must be optimised to avoid any risk of explosion. Clearly the time taken to start the ammonia conversion reaction throughout the platinum metals gauzes must be kept fairly short, otherwise explosive ammonium nitrate and nitrite compounds might form and build up downstream of the gauze pack during the start-up period.

The duration of the start-up is directly dependent on the initial catalytic activity of the platinum metals gauzes, especially on the first gauze that the gas passes through. In co-operation with ICPC RASc, GIAP has carried out a comparison of all available activation methods, based on the electrothermographic method described above. As a result an improved method for activating and regenerating the platinum metals gauze has been developed (27). The principle of this method is that radicals present in the hydrocarbon flame recombine on the gauze surface, when it is held at a temperature of 1000 to 1400°C.

The regeneration time increases with decreasing platinum content in the catalyst alloy, and is about 12 minutes/m² of gauze surface for the GIAP-5 alloy. This method does away with the need for the gauze to receive acid treatment, gives a 0.07 to 0.1 per cent reduction in platinum metals loss on regeneration, and reduces the start-up time by 5 to 10 per cent, and also increases the nitric acid yield by an average of 5 per cent within the first three days after reactor start-up.

In 1991 GIAP, in co-operation with the Lomonosov Moscow State University, completed the development of a method for the electrochemical activation of new platinum metals gauzes. The method includes anodic and cathodic polarisation of gauze in hydrochloric acid solution (28). This treatment removes contaminants from the surface of the gauzes, thereby increasing their active surface area from 20 to 120–240 cm²/g. Preliminary field trials carried out in the UKL-7 plant belonging to the Novgorod Azot IA have shown that two hours after reactor start-up the GIAP-5 alloy gauzes, activated by this method, reached about 98 per cent of their steady-state selectivity. This method will be used at the Ekaterinburg Non-Ferrous Metal Processing Works, where platinum group metals gauze is manufactured.

Finally, GIAP and ICPCCh RACs have jointly developed a device for bringing the ammonia oxidation reactors into operation, based on the application of linear electric heating elements. The device made it possible to do away with the bulky hydrogen-containing gas burners in the ammonia oxidation reactors (29). Previously these caused turbulence in the gas flow immediately up-stream of the catalyst and also unwanted pre-catalysis of ammonia to nitrogen on their surfaces (29). At present many of the UKL-7 plants are equipped with these electric ignition devices. In 1992 a device of this type was sold to Hungary.

Waste Gas Cleaning Stage

In the mid-1960s GIAP launched a project to develop the first large-scale nitric acid plant in the U.S.S.R. Designated UKL-7, this was designed using an energy and technology flow-

sheet which produced a closed energy circuit of the plant and used energy from the waste gas to compress the air fed to the system. Natural gas is used for two purposes in this flow-sheet: first as a fuel for preheating waste gas to between 450 and 550°C, and second as a reducing gas for the residual nitrogen oxides in the waste gas. The latter process is exothermic, and the temperature of the cleaned waste gas increases to between 700 and 750°C. This gas goes to the recuperative turbine of the gas-turbine plant. The compressor on the downstream side of the AK-72 plant also consists of a similar high-temperature gas turbine (1).

In the search for a catalyst for this process a number of different catalysts including: nickel, copper-nickel, chromium, nickel-chromium and palladium-nickel, were tested. However, all of them had one or other significant drawback, such as: low activity, carbonisation in an oxidising medium, or an ignition temperature which was too high.

A palladium catalyst supported on α -alumina granules was found to be the only catalyst to give 95 to 100 per cent removal of nitrogen oxides, the requisite stability and a relatively low ignition temperature of 420°C (1, 30). The optimum palladium content was 1.8 to 2.0 per cent, and this catalyst, with the trademark APK-2, has already been in operation in the CIS for about 30 years. It ensures waste gas, with an initial nitrogen oxides content of 0.3 per cent per volume, can be purified up to 0.005 per cent per volume. The minimum service life of the APK-2 catalyst is two years.

The UKL-7 and AK-72 plants are designed to use 3 and 8.5 tonnes, of the APK-2 catalyst, respectively, which is why investigators have been seeking to reduce the amount of palladium used at the cleaning stage. However, attempts at lowering the palladium content in the catalyst have so far been unsuccessful. An acceptable supported catalyst has not yet been developed either. However, another way of reducing the palladium mass embedding has been found.

GIAP and ICPCCh RASc have carried out theoretical and experimental investigations to find a way to reduce the amount of catalyst used. Their

investigations have shown that the exothermal process over the catalysts produces thermal and diffusion non-uniformities, that is the catalyst bed “breaks down” into “cold” and “hot” regions about the size of the catalyst bed thickness, even when an ideally homogenised flow of reactants is uniformly distributed over the bed of the APK-2 catalyst (31). These non-uniformities lower the efficiency of the APK-2 catalyst and result in its overconsumption. Based on these investigations our institutes have developed a new engineering approach to reduce appreciably these undesirable effects. This approach consists of partitioning, which is an innovative way of arranging the APK-2 catalyst and gives a minimum reduction of 33 per cent in the mass of this catalyst, used in the reactor, as compared to the design value. Catalytically inert components are used to partition the APK-2 catalyst. However, this does not increase the volume of the

partitioned catalyst bed in our catalytic element, making it fundamentally different from other engineering designs typically described, for example, in Reference 32.

The catalytic element which has been proposed ensures that the specified nitrogen oxides content in the purified gas, the purification capacity of the reactor, and the service life for the APK-2 catalyst are unimpaired. An additional benefit is improved stability for the operation of the reactor with respect to the waste gas purity level under varying natural gas duty. The labour and capital costs required to implement this development in an existing plant are very low. This engineering design has been used to advantage in a number of UKL-7 and AK-72 plants for about seven years. According to theoretical studies (31), this design shows promise for other exothermal processes which take place over a granular catalyst bed.

References

- 1 M. Bonne, N. D. Zaichko, M. M. Karavaev et al., “Nitric Acid Production in Large-Scale Single Units”, ed. V. M. Olevsky, Khimiya, Moscow, 1985, pp.94, 214
- 2 M. A. Miniovich, “New Active Mechanically Durable Catalyst”, GIAP 1, Publishing House GIAP, Moscow, 1947
- 3 M. A. Miniovich, A. L. Shneerson, V. A. Klevke et al., U.S.S.R. Certificate of Authorship No. 296,584, 1967
- 4 M. A. Miniovich, A. L. Shneerson, V. A. Arutyunyan et al., in: “Catalysis and Catalysts”, Naukova Dumka, Kiev, 1974, (11), 17
- 5 V. V. Barelko, P. I. Khalzov and V. I. Chernyshov, *Khim. Prom.*, 1987, (8), 506
- 6 M. M. Karavaev, *Khim. Prom.*, 1989, (1), 39
- 7 V. V. Barelko, P. I. Khalzov and V. I. Chernyshov, *Khim. Prom.*, 1989, (1), 40
- 8 N. V. Dobrovolskaya, M. A. Miniovich, D. A. Epstein et al., U.S.S.R. Certificate of Authorship No.300,057; 1969
- 9 M. M. Karavaev, A. P. Zasorin and N. F. Kleshchev, “Catalytical Ammonia Oxidation”, ed. M. M. Karavaev, Khimiya, Moscow, 1983, p.137
- 10 M. M. Karavaev, T. V. Telyatnikova, A. S. Savenkov et al., *Russian Patent* 1,220,193; 1984
- 11 E. A. Brustain, M. M. Karavaev, V. I. Vanchyurin et al., *Russian Patent* 1,676,142; 1990
- 12 I. E. Kalinichenko, E. S. Skvortzov, V. I. Chernyshov and V. M. Olevsky, *Khim. Prom.*, 1991, (4), 214
- 13 I. E. Kalinichenko, E. S. Skvortzov, V. I. Chernyshov et al., *Russian Patent* 1,614,634; 1988
- 14 A. S. Savenkov and V. S. Beskov, in “The Kinetics and Catalysis of Heterogenocatalytic Pressure Processes”, Vishcha Shkola, Kharkov, 1974, p.67
- 15 V. I. Chernyshov, E. S. Skvortzov, V. S. Lakhmostov et al., *Khim. Prom.*, 1976, (7), 529
- 16 E. S. Skvortzov, V. I. Chernyshov, V. M. Olevsky et al., *Khim. Prom.*, 1978, (12), 921
- 17 E. S. Skvortzov, V. I. Chernyshov and V. M. Olevsky, *Khim. Prom.*, 1989, (8), 597
- 18 V. I. Chernyshov, E. S. Skvortzov and V. M. Olevsky, *Russian Patent* 1,818,740; 1989
- 19 V. A. Ostapenko, V. I. Chernyshov, V. S. Beskov et al., *Russian Patent* 714,703; 1978
- 20 V. I. Atroshchenko and S. I. Kargin, “Nitric Acid Engineering”, Khimiya, Moscow, 1970
- 21 V. I. Chernyshov, V. V. Barelko, N. D. Zaichko et al., *Russian Patent* 1,102,183; 1982
- 22 V. I. Chernyshov, G. D. Nalivka, E. A. Brustain et al., *Russian Patent* 1,709,705; 1990
- 23 H. Holzmann, *Platinum Metals Rev.*, 1969, 13, (1), 2
- 24 N. A. Chvokin, V. Z. Pavelko, V. I. Chernyshov et al., *Russian Patent Appl.* 92-000,849; 1992. The decision of the Rospatent on the patent delivery 20.01.93
- 25 V. I. Chernyshov, K. Kozlowski, N. A. Chvokin et al., *Russian Patent Appl.* 92-005,760; 1992. The decision of the Rospatent on the patent delivery 21.01.93
- 26 T. Retmaniak, M. Marek, P. Polak et al., *Polish Patent* 107,510; 1977

- 27 S. V. Zyuzin, V. V. Barelko, V. I. Chernyshov et al., *Russian Patent* 1,573,594; 1988
- 28 E. A. Brustain, S. Y. Vasina, I. V. Lazaricheva et al., *Russian Patent* 1,807,608; 1991
- 29 S. V. Zyuzin, V. V. Barelko, V. I. Chernyshov et al., *Russian Patent* 1,476,677; 1987
- 30 V. E. Gorfunkel, in "Purification and Utilization of Sewage and Industrial Wastes", Institute of Technical Information, Kiev, 1964, p.93
- 31 Yu. E. Volodin, V. N. Zvyagin, A. N. Ivanova and V. V. Barelko, "To the Theory of the Spatially Nonuniform Stationary States (Dissipative Structures) Origin in the Heterogeneous-Catalytic Systems", Preprint, Chernogolovka, Institute of Chemical Physics of the Russian Academy of Science, 1988
- 32 Ch. N. Satterfield, "Heterogeneous Catalysis in Practice", McGraw-Hill Inc., New York, 1980

A Suitable Pin Material for Glass-to-Metal Seals

MULTICOMPONENT ALLOY CONTAINS PLATINUM AND PALLADIUM

Contact with an electronic device hermetically sealed within a canister is made by means of metallic pins that exit through a header, and are insulated from the header by a glass which also seals the canister. Such individual devices are formed into larger electronic assemblies by connections soldered to the conductor pins. These pins must have good strength and ductility, suitable conductivity, must be compatible with the usual solders, and form an hermetic seal with glass. Iron-nickel alloys are commonly used for this purpose, even though they are not wet readily by near-eutectic tin-lead solders. In current practice this disadvantage is overcome by plating the pin with nickel and then gold, but this metallised layer is prone to damage prior to the soldering operation.

In searching for a material with all necessary properties researchers at the Sandia National Laboratories, Albuquerque, have made a metallurgical study of alloy Paliney 7™, which is a multicomponent alloy sold by the Ney Company (D. R. Frear, J. R. Michael and P. F. Hlava, "Analysis of the Reaction between 60Sn-40Pd Solder with a Pd-Pt-Ag-Cu-Au Alloy",

J. Electron. Mater., 1993, 22, (2), 185-194).

Some of the properties of this alloy have been established by others, but there is no published information on the reaction between Paliney 7™ and tin-lead solder or on the reliability of the resultant solder joint. The current study has shown, however, that the wetting properties of 35 palladium-30 silver-14 copper-10 gold-10 platinum-1 zinc (weight per cent) are comparable to those of metallised gold-nickel, and result in good mechanical bonds. Also the multicomponent alloy retains ductility and strength after heat treatment tests designed to simulate the thermal conditions encountered during the formation of glass-to-metal seals. The intermetallic layer formed between the pin alloy and the 60 tin-40 lead solder consists mainly of PdSn₄, with platinum and gold substituting for palladium in the crystal structure; the structure is fine grained with extensive twin growth which prevents excessive brittleness. It is concluded that 35 palladium-30 silver-14 copper-10 gold-10 platinum-1 zinc is a suitable conductor pin material for glass-to-metal sealing applications in electronic packaging.

Platinum Foil in Ceramic Bonding

The solid state reaction that takes place between many ceramics and metals can be used to produce strong vacuum-tight joints which maintain their strength and durability even at elevated temperature, and the use of platinum foil for this purpose was reported here in 1981.

Reaction bonding to ceramics is best performed with platinum, which has a high melting point, is oxidation and corrosion resistant and therefore is the preferred metal for many bonding applications used in many hostile environments.

Now researchers at Lawrence Berkeley Laboratory, University of California, Berkeley, have developed a ceramic-ceramic joining method, partial transient liquid-phase bonding, that uses a thin foil of platinum to join copper

coated alumina surfaces (M. L. Shalz, B. J. Dalgleish, A. P. Tomsia and A. M. Glaeser, "Ceramic Joining. Part I. Partial Transient Liquid-Phase Bonding of Alumina via Cu/Pt Interlayers", *J. Mater. Sci.*, 1993, 28, (6), 1673-1684).

High purity platinum foil was placed between two layers of alumina coated with thin layers of copper. Partial transient liquid-phase bonding was achieved through this copper/platinum interface at 1150°C, yielding a platinum-rich interlayer and giving high-strength joints between platinum and alumina, at much lower temperatures than those required for conventional diffusion bonding. Flexure tests also showed that the obtained ceramic/metal interface strengths were higher than normally achieved for ceramics.