

Producing Electronic Compound Oxides

A DEMANDING APPLICATION OF PLATINUM APPARATUS

An increasing number of compound oxides in single crystal form are now being used as electronic materials for a wide range of applications. Generally the performance of these materials is closely linked to their purity, and considerable effort is being devoted to investigating the nature of specific impurities, their disposition within the crystal, their oxidation state and their effects on the properties of the crystal. In some instances noticeable effects occur at impurity levels below tenths of a part per million.

Stoichiometry control is an important aspect of the manufacturing process. For many reasons it is preferable to grow single crystals from pre-reacted compound oxides, rather than mixing the individual oxides immediately prior to crystal growing. In the former procedure, the composition of the residual melt does not vary appreciably even when it is topped-up with additional compound, and this enables more crystals to be grown before having to discard the residue.

At present there is a considerable demand for bismuth germanate (BGO), $\text{Bi}_4\text{Ge}_3\text{O}_{12}$, which is used in the detector system of the large electron-positron collider known as LEP-3, which is being built by the European Organisation for Nuclear Research (CERN) in Geneva. Johnson Matthey Chemicals Limited is supplying CERN with many tonnes of the polycrystalline raw material for issue to crystal growers throughout the world.

Other compound oxides used in single crystal form by the electronics industry include gadolinium gallium garnet (GGG), lead molybdate, lithium niobate, yttrium aluminium garnet (YAG) and zinc tungstate. These materials are also manufactured by Johnson Matthey Chemicals to meet the exacting specifications demanded by the users.

Both when preparing the polycrystalline feedstock and when growing the required single

crystals the composition of the container, and of some associated apparatus, is crucial to the success of the final product. With several of these compound oxides now being required on a tonnage basis it is clearly necessary to employ the most cost effective containment materials. Because of their high melting points, their mechanical strength and chemical inactivity with the oxide components at high temperatures, a number of platinum group metals and their alloys are used for this purpose. Of particular importance to this application is the fact that any noble metals from the apparatus entering the crystals are at extremely low levels, and it has been shown that they are unlikely to enter the crystal lattice.

For the most exacting applications at temperatures in excess of 1900°C iridium is employed. However, many processes are carried out at somewhat lower temperatures where other platinum group metals are more appropriate. Here there is a strong trend towards the use of containers produced from grain stabilised platinum or its alloys.

ZGS Platinum Crucibles

During the late 1960s and early 1970s Johnson Matthey developed a process which enabled a zirconia stabilised platinum material to be produced in large reproducible quantities, and at reasonable cost. Known commercially as ZGS platinum, the successful production of this material was a notable achievement in platinum metals technology. At the same time the fabrication problems were solved and today a family of grain stabilised materials has been developed based upon this process. From this family, a material possessing the required properties may be selected to meet a variety of high temperature containment needs, including crucibles for crystal growing.

In addition to enhanced high temperature strength, a major advantage of ZGS platinum

and its derivatives is their remarkable resistance to progressive contamination by reduced species, which is a major cause of eventual crucible failure, due to preferential diffusion of contaminants along grain boundaries. The increased grain boundary area conferred by the highly elongate fine grain structure of these materials provides a massive sink for contaminants, which increases the time before the critical composition of a low melting point or brittle intermetallic phase is produced.

With the increasing use of oxides of elements

such as bismuth and lead which readily form phases with platinum in the elemental form, particularly in high energy regions such as grain boundaries, the use of ZGS platinum has produced dramatic gains in terms of crucible durability and life. For example during the growth of bismuth germanate, lead molybdate and lithium niobate crystals the useful life of apparatus has been increased in the order of five or ten times, compared with that of conventional platinum apparatus.

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New Bimetallic Palladium Catalysts

HIGH EFFICIENCY HYDROCARBON PROCESSING

During the catalytic reforming processes used in the oil industry to increase the octane numbers of hydrocarbon fuels, the use of bi- and multi-metallic platinum based catalyst systems is well established. Now, it is reported that a new generation of bimetallic palladium catalysts has been developed for the hydrotreatment of hydrocarbon feedstocks where selective hydrogenation is required, for example the hydrogenation of acetylene to ethylene, or butadiene to butene-1 (J. -P. Boitiaux, J. Cosyns, M. Derrien and G. Léger, *Hydrocarbon Process.*, 1985, **64**, (3), 51-59). The use of these new catalysts helps to limit the occurrence of side reactions such as saturation of the double bond and olefin isomerisation and oligomerisation, as well as catalyst poisoning by sulphur containing feeds.

Procatalyse and Institut Francais du Pétrole have produced new improved bimetallic catalyst systems which comprise palladium and a second metal deposited on an appropriate support. The catalysts have been developed following mechanistic studies involving considerations of the relevance of the hard and soft acid/base theories of Pearson and the principles of organometallic ligands, in order to ensure the appropriate degree of binding of the unsaturated substrate molecules to the catalyst.

Preparative methods have been devised which result in direct interactions between the two metals present in the catalyst. Thus, methods used for the preparation of the catalysts include decomposition of a metallic salt by another metal previously deposited on the carrier, reduction of an organometallic compound by a first metal already deposited and

reduced, impregnation of the support with bimetallic clusters, coprecipitation of mixed oxides in the pores of the support and their subsequent reduction, deposition of a second metal on to another introduced previously in the oxide state as a support and using the strong metal support interaction (SMSI), and vapour condensation of the two metals on the support either in one step or two.

A palladium alloy catalyst system of this type has now been developed, for example, to hydrogenate the acetylene content (1.1 per cent) in ethylene streams using a new liquid phase process involving a recycled solvent. Similar processing techniques have also been used for the selective hydrogenation of both C₃ and C₄ streams, for the hydrogenation of propyne to propene, and for the removal of acetylenic material from butadiene, respectively.

All these processes have considerably increased life compared with conventional processes based on monometallic palladium catalysts, and palladium losses are considerably reduced in, for example, C₄ processing. Isomerisation of butene-1 to butene-2 has been limited by the addition of the second metal to palladium in the catalyst. The new palladium catalysts have been shown to give improved activity in the one-stage, selective hydrogenation of pyrolysis gasoline, where significant quantities of sulphur-containing impurities are present.

The authors conclude that their new generation of palladium catalysts meet the stringent requirements of the refining and petrochemical industries where economics dictate very high standards of performance.

D.T.T.