SPECIAL CERAMICS

The third international symposium on "Special Ceramics" was held at the British Ceramic Research Association during July 8–10, 1964. It was organized by Mr. P. Popper and followed the pattern of the 1959 and 1962 symposia. It is interesting to note the change in emphasis of the subject matter as progress in the nuclear power industry increases the demand for ceramic fuels and as advances in aircraft engine design lead to the search for new materials to withstand more rigorous operating conditions. The four half-day sessions of the symposium dealt with the preparation of non-oxides; pyrolytics and inorganic polymers; oxides and their electrical properties; and novel fabrication techniques and prospective applications as engine components. Ample time was allowed for discussion among the 170 delegates, who came from seven countries.

The symposium was opened by Dr. N. F. Astbury, director of the British Ceramic Research Association, who briefly reviewed the activities of the Association and its history, starting from an interest in technical refractories for the steel, glass and gas-making industries, later joining with the group working on pottery research, including electrical ceramics and chemical stoneware, and incorporating a building materials division. The youngest division, established to carry out investigations on special materials for future application in high-temperature engineering, was set up some ten years ago under the leadership of Mr. Popper. The visitors were invited to tour the Association's laboratories, where the many instruments in use included an electron microscope, electron probe microanalyser, direct reading spectrograph and mass spectrometer.

The first two papers, from the Atomic Energy Research Establishment, Harwell, considered the preparation and sintering of uranium nitride as a potential reactor fuel. Its preparation direct from the oxide would have economic advantages over its preparation from uranium metal or hydride, and Dr. J. B. Morris described work that he had carried out in co-operation with K. R. Hyde, D. A. Landsman, W. E. Seddon and H. C. J. Tulloch on the carbothermic reduction of uranium dioxide in a fluidized bed, in nitrogen, the carbon being either intimately mixed with the oxide or introduced as a hydrocarbon gas. The sintering to 92 per cent of theoretical density of uranium mononitride prepared by the reaction of nitrogen with uranium powder and the effects of oxidation, compaction, etc., on the sintering were described by Messrs. J. R. McLaren and P. W. M. Atkinson. General discussion of the relative merits of nitrogen and ammonia for nitriding various elements arose. Miss S. R. Billington (Morganite Research and Development, Ltd.) spoke of the investigations that she and Messrs. J. Chown and A. E. S. White had made of the sintering of silicon carbide and the possible mechanisms for transfer of material during this process, concluding that boundary-flow is operative. Messrs. J. Henney and J. W. S. Jones (Atomic Energy Research Establishment, Harwell) reported that investigations of zirconium carbide and the Zr–C–O system, preliminary to an investigation of the U–Zr–C system, had shown the existence of a single phase from $ZrC_{0\cdot6}$ to ZrC and had revealed two distinct oxycarbide phases, occurring at compositions approximately $ZrC_{0\cdot45}O_{0\cdot55}$ and $ZrC_{0\cdot5}O_{0\cdot5}$, with closely similar face-centred cubic crystal structures and no observed superstructure.

Pyrolysis has proved a useful method of making materials with negligible porosity and therefore high strength and chemical resistance and very low permeability. The method is well suited to the production of protective coatings and can also be used to provide bulk specimens. Pyrolytic silicon carbide was discussed in two papers. Dr. I. Mohyuddin reported that his investigation with Mr. P. Popper of the conditions for deposition of thick layers (3 mm) had shown that fine-grained silicon carbide of almost theoretical density and modulus of rupture 100,000 lb./in.^{2} could be deposited on a graphite substrate at 1,400° C from methyl trichlorosilane/hydrogen mixtures. Mr. R. Moreton (Ministry of Aviation, Farnborough) found that thick coatings of silicon carbide on molybdenum and tungsten rods tended to spall or crack due to a mismatch of thermal expansion coefficients, whereas thin coatings afforded protection against oxidation. Reaction between the silicon carbide and molybdenum was the cause of eventual failure, and Mr. Moreton suggested that a molybdenum/tungsten alloy of the correct expansion coefficient would allow thicker adherent coatings and greater protection.

There is an overlap between the usual definitions of 'inorganic polymers' and 'ceramics', and the relation between these was examined by Mr. P. G. Chantrell and Mr. P. Popper in considering the potentialities of inorganic polymers (classified here as chain compounds of high molecular weight) as electrical materials of moderate temperature stability and as intermediates in the preparation of refractory materials. That this classification was not generally accepted was demonstrated by a paper by Drs. P. Eckerlin, I. Maak and A. Rabenau (Philips, Germany), entitled "$LiPN_2$: A New Type of Inorganic Polymer". Dr. Eckerlin described a crystalline compound, derived from phospham, stable up to 1,000° C in vacuum and having a tetragonal structure formed of PN_4 tetrahedra which bears some resemblance to cristobalite. Dr. B. J. Aylett (Westfield College, London) discussed silicon–nitrogen polymers similar to the well-known polymers containing –Si–O– backbones and the problems of preparation to avoid the hydrolytic instabilities normally ascribed to them. He also mentioned some of the physical and chemical properties of the polymers produced.

Methods of quoting purity figures, as well as accuracy of analysis, came under discussion when three papers on high-purity ceramics were read, the point being made that many elements are not looked for in the analyses. Messrs. K. S. Mazdiyasni and C. T. Lynch (U.S. Air Force Materials Laboratory) advocated the use of organometallic compounds for the production of ceramic powders of ultra-high purity and small particle size, films and fibres, by thermal decomposition of the vapour, stressing the wide variety of compounds available. Fine zirconia powder and adherent refractory coatings on graphite have been produced from alkoxides. The process adopted by Messrs. G. M. Garner and F. C. Cowlard (Plessey-U.K., Ltd.) for the production of high-purity alumina was to prepare aluminium isopropoxide, purify this by vacuum distillation and convert it to alpha alumina. Mr. H. Bennett (British Ceramic Research Association) reviewed the difficulties associated with analysis of alumina ceramics and gave details of possible analysis procedures for different levels of impurity.

The contribution by Dr. L. S. Williams (Commonwealth Scientific and Industrial Research Organization, Australia) on infiltrated oxide cermets was read in his absence by Mr. D. E. Lloyd. Further progress had been made in the infiltration of alumina and other oxides with silver and its alloys and in the combining of impact strength and creep resistance with thermal shock resistance, for possible application as gas turbine components. Prof. W. W. Kriegel (University of North Carolina) described how he, Hayne Palmour III and D. M. Choi had produced and varied the properties of pore-free polycrystalline magnesium aluminate spinel, which he considered as a possible high-performance structural ceramic on account of its chemical and thermal stability and multiple {111} <110> slip systems.

Three of the papers discussed the electrical properties of alumina. Drs. T. Matsumura and M. Laubitz (National Research Council, Canada) had calculated the ionic transport number from E.M.F. measurements on an $O_2(p_1)$, $Pt/Al_2O_3/Pt$, $O_2(p_2)$ galvanic cell at temperatures 700°–1,200° C and pressures 10^{-2} – 1 atm. Dr. Laubitz reported that their results were in agreement with the work of Schmalried but disagreed with some other diffusivity measurements. This type of experiment can throw considerable light on the mechanism of grain boundary diffusion. Dr. V. Daniel (Electrical Research Association, Leatherhead) described her work with Mr. M. Rogers on the degradation of ceramic insulators at high temperatures and the effects of various electrode materials, with particular reference to the rectifying barriers formed at electrode–ceramic interfaces. Dr. A. J. Moulson had also considered, with Messrs. W. R. Phillips and P. Popper, the degradation of alumina ceramics, concentrating on measurements of the diffusion of the two commonest heater-current metals, nickel and chromium, into various grades of alumina and the effect of their oxide additions on the resistivity. Some discussion of methods of measuring high-temperature resistivity to avoid surface and apparatus effects ensued. In an investigation of the effect of heat on pure single crystals of rutile, Mr. M. G. Harwood (Mullards, Ltd.) found that the d.c. stability at 150° C was raised whereas the a.c. losses were not correspondingly improved, indicating that different centres were responsible, and that only some tri- and tetra-valent cations improved the d.c. stability.

Thermal conductivity and emissivity are of importance in high-temperature applications, and materials of low friction are required for high-temperature bearings. Dr. R. W. Powell presented some results which he and Mr. R. P. Tye had obtained at the National Physical Laboratory, using both the longitudinal heat-flow and thermal comparator methods for measuring the thermal conductivity of carbides and borides, and suggested that these should be considered as metallic alloys rather than covalent compounds. Mr. J. C. Titus-Glover described emissivity measurements at 1,500°–2,500° C made with Dr. V. Croft at the University of Sheffield using a double parabolic arc image furnace and low-resolution spectrograph with a silicon cell radiometer. At the Cavendish Laboratory, Cambridge, Drs. C. A. Brookes and M. Imai had investigated the frictional properties of reaction-sintered silicon nitride and silicon carbide. These compared well with metals and the coefficient of friction was independent of load. Surface finish was important for wear resistance.

In the session on fabrication techniques, Dr. S. Scholz described a neat hot-press that he and Dr. E. Roeder had used at the Philips Laboratory in Germany. It reached 3,200° C and 1,000 kg/cm² and accurate densification/time measurements on the small samples were recorded. Some of the limitations to hot-pressing for industrial applications have been overcome by Dr. G. S. Gruintjes and Mr. G. J. Oudemans (Philips Research Laboratories, Eindhoven), who described a new technique for continuous hot-pressing that had produced long rods of both metals and ceramics. Intense collimated plasma-electron beams of powers up to 5 kW had been obtained by Messrs. J. W. Isaacs, C. W. A. Maskell and J. D. L. Harrison at the Atomic Energy Research Establishment, Harwell, from robust, hollow cathodes without filaments, and Mr. Harrison discussed methods of controlling the energy and size of the beam and applications to the melting of ceramics.

Turning to future applications, Dr. E. Glenny's paper "Ceramics and the Gas Turbine", read by Mr. R. Smith (National Gas Turbine Establishment), attributed lack of early success in applying brittle materials in gas turbines to inadequate effort, arising from insufficient incentive, and to the failure to re-design components to suit the new materials. The usefulness of materials at present available for heat exchangers, nozzle guide-vanes and coated turbine blades was discussed. Mr. N. R. Hemming (Bristol Siddeley) spoke of the need for refractory materials combining strength, toughness, lightness and oxidation resistance for use in air-breathing ramjet engines, which could advantageously be used in hypersonic aircraft capable of speeds of Mach No. 7, where wall temperatures would rise to 2,100° C.

On behalf of the visitors, Dr. W. W. Shaver of Corning's, New York, thanked the British Ceramic Research Association for its hospitality. Following Dr. Astbury's formal closure of the symposium, the visitors were able to inspect some of the work being done at the Association's laboratories.

The *Proceedings* of the symposium will be edited by Mr. P. Popper and published by Academic Press, in the spring.

S. N. RUDDLESDEN

PHENOLICS IN NORMAL AND DISEASED FRUITS AND VEGETABLES

THE phenolic compounds of fruits and vegetables, their relationship to browning, their changes when plants are infected, and their role in resistance of plants to disease constituted the symposium topic for the fourth annual meeting of the Plant Phenolic Group of North America, at the Central Research Laboratories of the United Fruit Co., Norwood, Mass., during July 23–24.

The symposium opened with three papers on dopamine (3,4-dihydroxyphenylethylamine) based on research by the United Fruit Co. Dopamine, a major phenol in banana, is readily oxidized to form melanin. E. H. Buckley discussed the periods of dopamine accumulation, content, and distribution in banana peel and its biosynthesis via tyrosine and tyramine throughout the plant. J. K. Palmer outlined the enzymatic oxidation of dopamine to melanin by banana polyphenoloxidase (PPO) and the unique substrate specificity spectrum of banana PPO, with dopamine the most reactive by far. The inhibition of banana PPO *in vitro* was stressed. Reducing agents apparently worked by three different mechanisms, while the varied inhibition patterns of chelation agents indicated that other mechanisms were involved as well as chelation. Finally, M. E. Mace discussed the relationship between *Fusarium* wilt infection in banana roots and the phenolics present. Anatomical and histochemical investigations, as well as experiments *in vitro* and *in vivo*, were presented in support of the hypothesis that, in infected banana roots, oxidized dopamine mediates the conversion of tryptophan to indolyl-3-acetic acid. The IAA then induces localized tyloses that block the vascular elements and entrap spores, and thereby localize infection.

The first session was completed by a discussion of the anthocyanins of grapes by A. D. Webb (University of California, Davis). Only since the advent of paper chromatography has the complexity of anthocyanins in grapes been appreciated. Completely satisfactory methods for isolating the pigments in natural form are not yet available. Wines made from hybrids of *Vitis vinifera* with disease- and cold-resistant native American species of grape can be detected by chromatography; this test is of legal impor-