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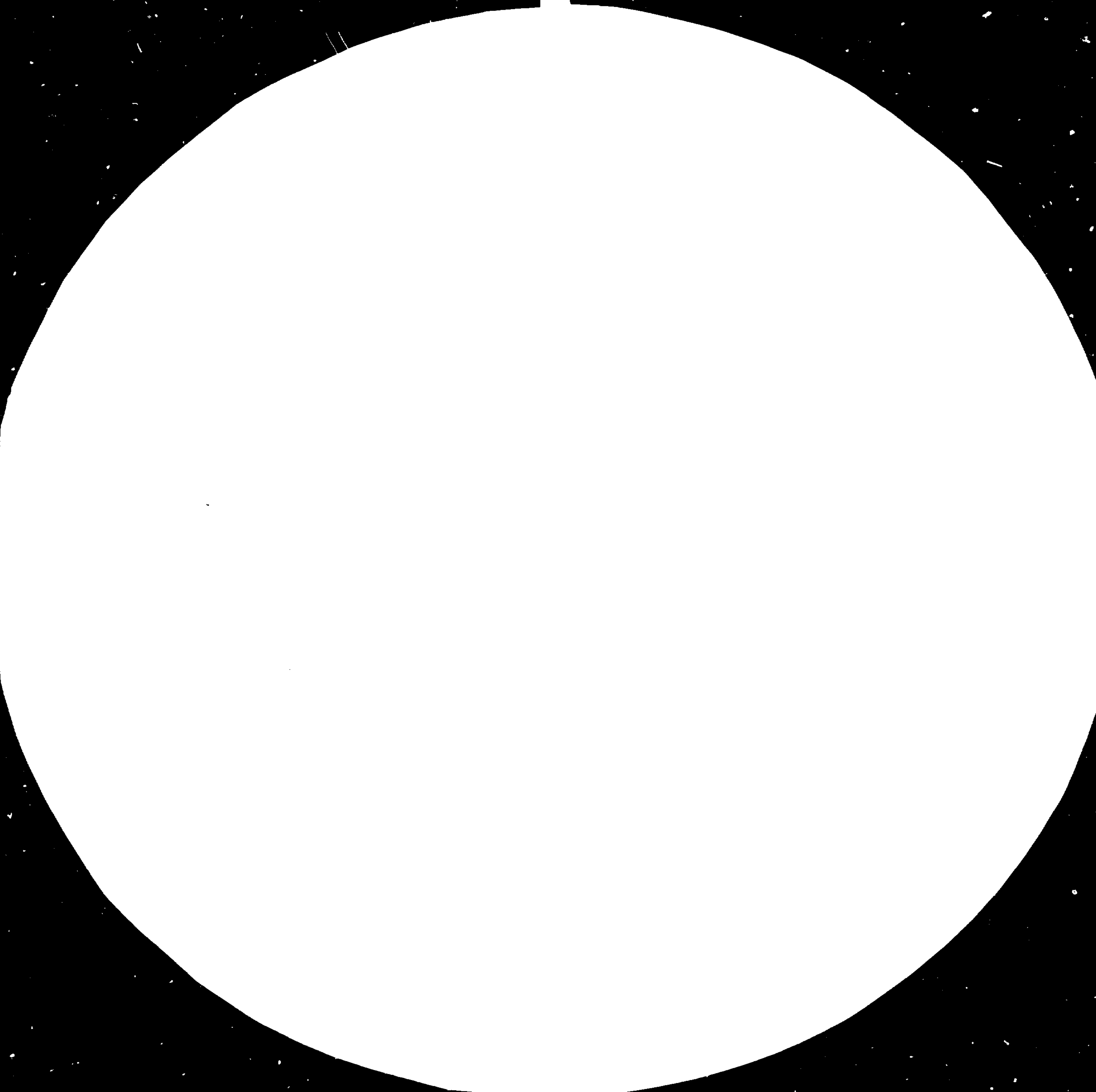

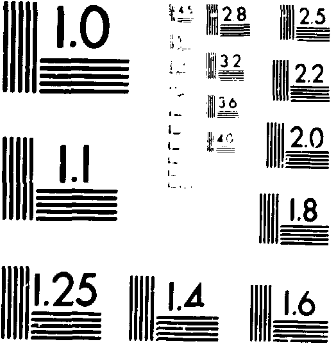

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UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION

Advances in Materials Technology: MONITOR

14041

Issue Number 2 August 1984

Dear Reader,

This is the second issue of UNIDO's state-of-the-art series in the field of materials called Advances in Materials Technology: Monitor. This issue is devoted to new ceramics and is addressed to a select target audience of policy makers, scientists, technologists and industrialists in developing countries.

In each issue of this series, a selected material or group of materials will be featured and an expert assessment made on the technological trends in that field. In addition, other relevant information of interest to developing countries will be provided. In this manner, over a cycle of several issues, materials relevant to developing countries could be covered and a state-of-the-art assessment made, hopefully every two years.

New ceramics, also known as fine ceramics, high-performance ceramics and advanced ceramics, are receiving increased attention as many scientists see ceramics replacing high-performance metals and plastics. This issue contains four articles written by experts in the field of ceramics. A current awareness section includes information on new products, new materials, new processes, market trends and news from developing countries. A list of publications and information on meetings in this field are also contained in this issue.

In preparing the monitors, the Technology Programme is receiving valuable help from experts in and outside UNIDO. We hope to have their co-operation in our future issues as well. Mr. Edward Epremian, Special Technical Adviser and Special Assistant to the Executive Director of UNIDO on Energy has been providing valuable suggestions on the substantive aspects of this series of monitors.

The UNIDO secretariat would welcome information on materials and suggestions on the format and content of this issue from readers.

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Director
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CONTENTS

CURRENT AWARENESS

New Products

New fine ceramic board

Toshiba of Japan has developed a new fine ceramic board for semiconductor application. The thermal conductivity of the ceramic is five times greater than the conventional alumina board. The base was developed to accommodate large amounts of thermal dissipation in large-scale integrated circuits, which consume great amounts of power. The new base is prepared by the ambient pressure sintering of fine aluminium powder. The new board increases miniaturization and reliability, has about 1.5 times the dielectric strength and twice the mechanical strength of an alumina base. The thermal expansion coefficient is similar to that of silicon. The new ceramic can be used to produce pressure-resistant, high-speed, high-scale integrated circuit boards. The technique to develop the new ceramic involved the development of a yttrium oxide for a sintering aid to densify the sinter and make possible mass production by ambient pressure sintering, the development of the necessary circuit-wiring technology and high-grade homogeneous aluminium nitride production and its purification, developed through a co-operative effort with Toshiba Ceramics. (Denki Shimbun (in Japanese), 29 February 1984, p. 5. Copyright 1984 by Nihon Denki Kyokai.)

A new ceramic press

Ram Products of the United States has designed a ceramic press that uses precision dies for pressing ceramic ware and lowers production cost, set-up time and die weight. Plaster and ceramic dies are housed in large steel or cast-iron cases. In 1983 Ram developed a 25-ton operator-oriented press that offers advantages and features of larger Ram presses. This smaller press is more easily and directly controlled by the operator. A small-scale production line using a Ram press along with automated procedures for handling the materials is presently being constructed. The operator activates the mixer or pug mill, causing materials to move between them, and bringing materials from the extruder through an automatic cut off and up to the press. (Ceramic Industry, March 1984.)

Ceramic turbo-engine

Hino Motors, Ltd. of Japan has succeeded in developing a ceramic turbo-engine with the highest thermal efficiency of any diesel engine to date. The 8.8 litre displacement engine has a thermal efficiency of 50 per cent, which corresponds to fuel efficiency, and a maximum power output of 380 hp (up to 20 per cent), corresponding to a 19-litre engine without turbo. The new engine was made possible by new technology, including (1) the use of large amounts of ceramic composites in engine parts, (2) provision of a two-stage turbo, and (3) electronic control of fuel injection. The ceramic composite material combines the strong toughness of steel and the superior refractory qualities of ceramics. The process consists of inserting sintered silica in combustion chamber parts (pistons, cylinder liners, valves, cylinder heads and exhaust ports) and spraying ceramic materials on surfaces. Ceramics are also used for parts of the compressor, an auxiliary device. There is no necessity for a radiator, cooling fan or water pump because an engine cooling system is not necessary. The high temperature within the engine does not prevent smooth operation and, because of the insulating quality of ceramics, the temperature outside the engine is not excessive. In testing ceramic engines previously, energy was allowed to escape as high-temperature exhaust gases. Hino has developed a mechanism to use the high temperature and high-energy gases to operate a two-stage turbo. The first stage is an ordinary supercharger and the second stage uses a fluid clutch to add impetus to the crankshaft. The high temperature and energy of exhaust gases are recovered while passing through the two turbos, increasing the engine's explosive and rotational power. (Nikkei Sangyo Shimbun (in Japanese), 14 October 1983, p. 1. Copyright 1983 by Nihon Keizai Shimbunsha.)

Turbine application studies

Ceramics will increasingly be used in gas turbines. "In the last decade a number of practical studies in engines or engine component test rigs have had the primary objective of demonstrating that ceramic components can survive in the gas turbines, following earlier recognition and advocacy that such exploratory studies might be successful and advantageous, because ceramics could be developed with high strengths and low coefficients of thermal expansion which would minimize thermal stresses. Four investigations in particular have been of great value because details of the failures as well as the successes have been openly available. These have been four projects in the USA: (a) at the Ford Motor Co., (b) at Westinghouse Research Laboratories, (c) at the Garrett Corporation and (d) at Solar."

"The Ford project had the objective of demonstrating for a small vehicular gas turbine the short term durability (200h - 175h at 1055°C and 25h at 1372°C) of a wide variety of ceramic components, to achieve a 20 per cent improvement in specific fuel consumption (SFC) and a 50 per cent improvement in specific air consumption, at typical pressure ratios of 4:1 and 6:1 by increasing temperature from the limit of 1800°F (982°C) necessitated by the use of uncooled superalloys, to 2500°F (1371°C) for ceramic parts. Static components included an RBSN nose cone (diverting hot gases from the combustor into the turbine), both RBSN and RB silicon carbide (RBSC) stator vane assemblies, two types of RBSN tip shroud rings and an RBSC combustor. A ceramic rotor assembly, consisting of a HPSN hub bonded to an injection moulded route RBSN rotor blade ring was also hot spin tested with, eventually, success after a number of failures, most of which were due to problems with metal parts of the load-transference curvic coupling becoming overheated. The culminating demonstration comprised operation at speeds of up to 50000 rpm, for 200h at a rim temperature of 1000°C and blade temperatures of 1200°C. The application of ceramic rotary regenerative heat exchanger materials of the lithium alumium silicate (LAS), aluminium silicate (AS) and cordierite (MAS) types was investigated, and 5 AS regenerators were demonstrated successfully with inlet temperatures of up to 800°C for over 10000h, and four up to 1000°C for over 5000h. During this work, in which many severe problems and disappointments as well as many successes occurred, an effective liaison between design evolution and innovation on the part of engineers and materials improvement and quality assurance efforts by ceramists was apparent. Particularly helpful to the work was the in-house development of many aspects of the ceramic processing such as the injection moulding of one-piece blade rings, and their attachment by hot pressing to the fully-dense hub."

"The Westinghouse work was aimed at large gas turbines used for electric power generation, and concentrated on the design and testing of large stator vanes. HPSN aerofoils were clamped (by a special concentric spring device to ensure a uniform spring rate) in HPSN shoe root fixtures, which were then thermally insulated by glass ceramic plates from the spring. After initial difficulties in obtaining the complex parts properly dimensioned, testing showed that HPSN parts could survive typical work schedules and cooling ramps without failure. The failure of a metallic combustor in the test rig, probably by overheating, caused an unintended severe projectile impact test, which left most of the HPSN blades uncracked although impacted by molten or near-molten parts of the combustor, silicon carbide vanes failed catastrophically. A redesign of the combustor gave a steeper temperature gas stream traverse, causing some thermal stress cracking of HPSN blades in further tests. The work showed that with previous engineering experience, reliable ceramic component usage in large power turbines was practicable, and identified thermal stress as a possible failure mechanism with HPSN."

"The objective of the Garrett work (which commenced in 1976) was to demonstrate that a moderate-sized gas turbine (746 kW) with a ceramic hot section could operate essentially uncooled at an average turbine entry temperature of 1197°C (peak temperature 1367°C), a 195°C increase over an equivalent (533 kW) engine operating with metallic components, giving a 40 per cent increase in power and a 10 per cent increase in specific fuel consumption. The design involved the use of over a hundred ceramic parts, varying from small rotor blades and stator vanes to large cylindrical shrouds. HPSN was used for the rotor blades since these were the most highly-stressed components. A considerable amount of material characterization work was carried out, in which a problem of exposure to high temperature weakening the HPSN was identified. An oxidation treatment of 50h at 1800°F (982°C) was found to substantially diminish both this and also machining and billet orientation effects on strength. Rotor blades were proof tested by spin testing them individually at speeds 30 per cent greater than the design speed; the failure probability based on the material characterization data was 3 per cent; in fact 6 out of 205 (2.94 per cent) failed the spin test. A stress maximum was calculated for the static parts as 149 MPa 115 seconds after engine start assuming a combustion hot spot of 1371°C; the mean strength of the RBSN tried was over 200 MPa at that temperature. A total of 19 rig tests of the static structure were carried out, the last a 10h test to 927°C average turbine entry temperature (TET) and an aerodynamic loading 20 per cent greater than that of the design, and which included 22 transient cycles. A rotor vibration problem was solved by changing the blades in the two stages from 21 and 21 to 19 and 17, and the rotor was operated successfully to 45000 rpm and 927°C. Twenty-seven engine tests were completed; some successfully, some in which chipping or cracking of the static components was found on disassembly, and finally a test at 41730 rpm and 1204°C which ended in complete engine failure. Prior to this one test had included 23 starts and 20h of up to 31000 rpm and 927°C TET; another test (with 19/17 blade set) included three 1 and 2 hour runs to the design 41730 rpm and 1204°C TET. Substantial performance benefits were demonstrated of 30 per cent increase in shaft power, and 7 per cent in specific fuel consumption. The catastrophic engine failure were ascribed to contact stresses at metal - and ceramic - ceramic interfaces. Subsequently a test apparatus was built to study contact load effects, and sliding and biaxial contact loads were shown to cause failure although uniaxial loads did not. A tensile stress high enough to cause failure was shown to occur in a shallow (100 μm) region behind the moving load, giving failure when the area was next loaded. As this indicated a significant redesign of the static structure, the work was largely discontinued, in favour of work on a new ceramic component engine (the AFML/APL engine). However a TF6 engine was modified to test a ceramic bladed first blade rotor with metal static parts. Two 7.5h tests with 12 minutes at 1204°C were successfully conducted, and in a further more severe test included two 12 minute periods at 1210°C to 1240°C, which gave 13 per cent more shaft power and an improvement of 6 per cent in SFC, although the tip clearance was greater than for a metal engine, and could be reduced to improve efficiency."

"In a new collaborative programme between Garrett and Ford, an advanced gas turbine (AGT 101) is being developed with ceramic hot path components, operating to 1371°C and 100,000 rpm rotor speed. The AGT 101 has a single-stage radial inflow turbine on a common shaft. Ceramic part tests in the power system are scheduled for late 1983. A sintered RBSN non-bladed rotor has been successfully spin tested at 134000 rpm. A bladed rotor had been spin tested at 102,000 rpm, a 716 m/s tip speed, and a peak stress of 233 MPa."

"Solar, San Diego have worked on the application of ceramics in a 10 kW gas turbine. Erosion of 713L superalloy in dusty conditions could give blade lives as short as 68h. Tests showed that HPSN resisted such erosion far better. HPSN vanes and RBSN shrouds survived over 500 engine-type cycles. In a 60 kW turbine test with 44 ng/kg air of -140 mesh SiO_2, a metal vane receded 12 mm, but HPSN was unaffected. Complete survival of ceramic nozzles and shrouds in an engine was demonstrated."

"At Pratt and Whitney, the performance of HPSN blades held in a metal disc which was hot-forged around the blade roots was assessed. A number of successful engine simulated tests were completed (e.g. 50h, including 10 cycles to 45,000 rpm and 1232°C with a 30-bladed rotor). At Detroit Diesel Allison ceramic parts, including silicon carbide stators, have been tested for a 261 kW (350 HP) regenerative two-shaft 1241°C TET truck turbine; over 100h of experience at 1038°C TET had been accumulated by 1979, with over 25h road experience with ceramic vanes in the engine in a vehicle on the road."

"In the UK, Rolls Royce Leavesden are working with ceramics in three gas turbine applications: a main shaft gas bearing, an HP turbine shroud and HP turbine blades. The gas bearing has now run over 30h, using Syalon shells against chromium oxide coated INCO 718. The monolithic HPSN shroud has accumulated over 75 test hours, performance is very encouraging, and 150-250h testing should complete in Spring 1984. Experiments are proceeding with abradable coatings. Fully machined HPSN blades have been made ...."

"In the Federal Republic of Germany, three firms have projects backed up by extensive ceramic processing R and D in industry, technical institutions and universities. Volkswagen are developing a 100 kW2 shaft turbine, the power turbine of which has a metallic disc with ceramic blades; the gas generator turbine has a monolithic ceramic rotor. Daimler Benz have a 150 kW design with a monolithic rotor of HPSN; MTU's project is with a 300 kW design, with a metallic disc and ceramic blades. In addition to these components, ceramic combustors are under development, and good progress is being made; first successes were reported with a RBSC combustor. A great deal of reiterative design work has been done on ceramic stators with testing ranging up to 1325°C, including inserted blade and bonded design, with externally or internally-slotted rings, and even hollow blades; high quality RBSN is the preferred material. A monolithic HPSN rotor has been tested successfully at 1000 Hz and 1250°C, and 833 Hz and 1350°C. A radial turbine has been operated hot at a tip speed of 340 m/s. (Extracted from D. J. Godfrey, "The use of ceramics for engines", Materials and Design, v. 4, June/July 1983.)

Ceramic turbo-chargers

Mitsubishi Heavy Industries (MHI) and Ishikawajima-Harima Heavy Industries (IHI), two of Japan's biggest turbo-charger makers, began making sample ceramic turbines for domestic and overseas car companies last summer. MHI has announced plans to begin mass production this fall, predicting that its ceramic turbines will be mass-produced within three to four years. "Ceramic turbines are about 40 per cent lighter than the conventional nickel alloy type. It takes less exhaust gas to rotate them, so the turbo-charger kicks into action sooner after the engine starts, significantly improving acceleration."

"The material that MHI and its arch rival, Ishikawajima-Harima Heavy Industries (IHI), fabricate from is silicon nitride, which is stronger than the other potential candidate, silicon carbide. The crucial stage in manufacture is firing. As the moulded part can lose anything up to 20 per cent of its volume in the oven, the trick is to get its dimensions as accurate as possible. Previously, removing pores required further processing, in a hot press. However, hot pressing is prohibitively expensive, and both companies claim that the need for it has been eliminated."

"Powder purification, moulding and baking are done to order by specialist ceramic companies, such as NGK Insulators (for IHI), and Asahi Glass and Kyocera (for MHI)."

"IHI has developed two types of shaft: one entirely ceramic, the other half ceramic, half metal. Both are equally strong."

"The problem with the all-ceramic shaft is that a thread must be machined onto the end (difficult because the material is hard and brittle) so it can screw onto the metal air-intake compressor. Compensation must also be made for the different thermal expansion ratios of ceramics and metal. The problem with the half-and-half shaft is to connect the metal to the ceramic without breaking it." MHI has decided to use a metal shaft joined to the turbine wheel by a ring of cobalt alloy that is welded to the metal shaft and has a similar thermal expansion coefficient to that of the ceramic shaft. "The final, crucial factor in turbine development is the price of the silicon nitride powder itself. Theoretically, being just "mud and air", it should be very cheap. Today, however, because it needs expensive purification, the powder costs about £10 a kilogramme. If ceramic turbochargers catch on, the price should drop dramatically as big-batch production evolves to meet demand." (Extracted from Bob Johnstone, "Japanese companies deliver sample turbochargers", New Scientist, 26 January 1984, p. 17.)

New Materials

Translucent aluminium nitride ceramic

Tokuyama Soda of Japan has developed a translucent aluminium nitride ceramic for integrated circuits and optical materials that is five times as thermally conductive as alumina ceramics. Super-pure aluminium nitride powder is sintered at atmospheric pressure into ceramics, allowing light to pass through. The ceramic has an oxygen content of about 1 per cent and positive iron impurities of 300 ppm. (Japan Chemicals, 3 May 1984, p. 7.)

More efficient ceramic alloy

Lucas Cookson Syalon of Solihull, England has developed a new ceramic that is more efficient than the metal alloys currently available on the market. This alloy is made up of silicon, alumina, oxygen and nitrogen. It is hard as diamond and can be moulded, extruded, pressed or cast into a range of components and tools. It retains its strength up to 800°C. Applications include lathe inserts that are stronger than tungsten carbide, welding location pins that last more than 700 times longer than conventional materials, seals with practically non-existent wear and long-lasting car engine tappets. (Design News, 7 May 1984, p. 15.)

New silicon nitride material

ASEA, Inc. (General Electric Company, Inc.) of Sweden is developing a silicon nitride material using the HIP (Hot Isostatic Pressing) method to compact ceramic powder under high pressure and temperature. The shaped body is coated by a glass layer under very high argon pressure during the process.

Sankvik, Inc. is developing a silicon nitride alloy called SiALON, which is said to be excellent for cutting processes. (Kemisk Tidskrift (in Swedish), January 1984.)

Zirconic ceramic

To overcome fragility, the weakest point of fine ceramics, Toyo Soda Manufacturing Co., Ltd. has developed a zirconic ceramic with the greatest bending strength yet possible, amounting to 250 kg/sq. mm, by far exceeding the existing maximum strength of 170 to 180 kg/sq. mm, and two or three times stronger than silicon carbide and silicon nitride, which are the primary basic materials of engineering ceramics used for components. In order to control cracks to a minimum, powder is mixed with plural ceramics, with zirconia forming the main portion. The particles are then refined to a submicron (1/10,000 mm) unit. In order to prevent cracks from spreading, the sintering additive yttria is mixed together with zirconia and a hot hydrostatic pressure press (HIP) is applied to reinforce its strength. The company will make the research data available to the public at the annual convention of the ceramic association to be held in May 1985. (Nihon Keizai Shimbun (in Japanese), 19 October 1983, p. 1. Copyright 1983 by Nihon Keizai Shimbunsha.)

New ceramic-reinforced composite material

Showa Denko and Tateho Chemical Industry have jointly developed a ceramic-reinforced composite material and the technology necessary for its production. The material is prepared by the addition of whiskers to a few per cent by weight of alumina or zirconia ceramic material. The mixed ceramic material is plasma-spray coated on a substrate to form a reinforcing oxide coating. By this method there is a two- to three-fold improvement in thermal shock resistance over that of conventional ceramic spray coating, while adhesion improves between 130 per cent and 140 per cent. As a result, the coating can be applied to automobile engine parts and to heat resistant and high-temperature corrosion-resistant parts. The products resulting from the use of these materials and this technique have showed outstanding results in thermal shock resistance tests and in peeling resistance tests, compared to those products that use the conventional ceramic spray-coating technique. Until now, automobile engine parts, such as gas turbines and cylinders, and steel or aluminium water heaters, which require heat- and high-temperature-corrosion resistance, were spray-coated with ceramics. However, there were problems with thermal shock resistance and peeling resistance. (Nikkan Kogyo Shimbun (in Japanese), p. 7. Copyright 1984 by Nikkan Kogyo Shimbunsha.)

New transparent PLZT ceramic

The Inorganic Material Research Laboratory of the Science and Technology Agency of Japan has developed a ceramic material PLZT, lead-lanthanum-titanate-zirconate. This material has an improved light transmittance and can be used as optical elements, such as optical shutters and optical memories. PLZT, which changes its bifringence when an electrical potential is applied, is a piezo-electric ceramic. When a light beam is passed through a cystalline material, which vibrates the beam, the beam splits in two directions. The bifringence is the difference between the two refractive indexes of the split beams. Although the difference is very small, by utilizing that optical loss effect, the light, which is momentarily shut off, acts as an optical shutter or an optical memory. PLZT also can be used as a colour filter by passing a light with a given wavelength through it. To prepare the new PLZT, a solution containing lead, lanthanum, titanium and zirconium is prepared and an oxalic acid-ethanol solution is added while stirring. The precipitate is hot-pressed for about 10 hours at 1000°C and 600 kg/cm pressure. In the conventional method, the final process takes 20 hours at 1200°C. An advantage of the new process, therefore, is energy conservation. The PLZT that is commercially produced by Motorola of the United States has a transmittance of about 40 per cent at 1 millimeter thickness, whereas the PLZT developed by the Inorganic Material Research Laboratory has an 85 per cent transmittance at a thickness of 2 millimeters. (Nikkan Kogyo Shimbun (in Japanese), 17 February 1984, p. 24. Copyright 1984 by Nikkan Kogyo Shimbunsha.)

PSZ developed in Australia

The Commonwealth Scientific and Industrial Research Organization (CSIRO) of Australia has developed a partially stabilized zirconia (PSZ) possessing high strength, mechanical reliability and toughness. Zirconia in its pure form is chemically inert but is a poor ceramic because of a mechanically-damaging phase transformation that occurs in its crystal structure when it is cooled after firing. The crystal structure is cubic at very high temperatures, transforming to tetragonal at intermediate temperatures and to monoclinic at lower temperatures. At the lower temperature transformation, there is a 4 per cent volume expansion of the crystal. By alloying zirconia with oxides of calcium, magnesium or yttrium, a more stable cubic crystal form is retained. This form - fully stabilized zirconia - still is not resistant to thermal shock. CSIRO has developed a partially stabilized zirconia, which has high strength, mechanical reliability and toughness and can be used where abrasion resistance to fine particle damage is required, for example in slurry erosion, in scuffing and metal extrusion operations where good friction properties are required, on high temperature diesel engine components, and in highly corrosive environments where chemical stability is a prime requirement. ("CSIRO develops zircon for engineering ceramics", Mining Journal, v. 302, no. 7751 (9 March 1984), p. 157.)

Ceramic paper

Nippon Chemical Industrial Co., Ltd. of Tokyo, the Meisei Chemical Industry Co., Ltd. of Kyoto and the Shikoku Paper Co., Ltd. of Tokyo have developed a low-temperature calcinable ceramic paper (also called pottery paper). A mixture consisting of pulp, clay, and a special sintering agent is formed into paper, which can be folded, cut or formed freely into any desired shape. The resulting green is fired to burn off the pulp, and the clay becomes ceramic. This product can be widely used in arts and crafts as well as in industry. During the conventional method of preparation, the firing temperature is above 1200°C, making shape retention after firing difficult. These companies have developed a new sintering agent which lowers the firing temperature and also has a fusion effect. The use of the sintering agent permits the lowering of the ceramic firing temperature to 700°C to 1000°C, which is 300°C-400°C less than the temperature of conventional firing, so that the original shape is retained. A conventional type of furnace can be used and energy can be conserved. Utilizing this technique, shaped ceramic products such as porous ceramics, heat-resistant materials, and absorbents can easily be produced. (Nikkan Kogyo Shimbun (in Japanese), 22 February 1984, p. 8. Copyright 1984 by Nikkan Kogyo Shimbunsha.)

Ceramic-ceramic composites

In Cerasep ceramic-ceramic composites developed by SEP, the France-based European Propulsion Company, the cracking and rupture process is very different from that in both common ceramics and in certain other composites. Instead of direct, rapid and relatively low-energy crack propagation, a far more complex crack propagation is observed in which the fibres simultaneously act as reinforcement and as a buffer or deflector. As a result, much more energy is needed to break such a part, making the composites resistant to mechanical impact. The material is also less sensitive to internal flaws, thus improving service safety and production reproducibility. Some Cerasep ceramic-ceramic composites also offer resistance to thermal fatigue. After 300 cycles at temperatures ranging from 100°C to 1100°C, with very brutal air-jet cooling, no crack appeared, even on "wedge" specimens with a very acute angle. Cerasep composites have a bending strength similar to that of sintered ceramics. They retain their bending strength at temperatures even exceeding 1200°C, and their resistance to corrosion is very good at such high temperature. The techniques developed by SEP to manufacture the composites are based on pyrolysis of ceramic precursors after impregnation of a ceramic-fibre preform and vapour phase infiltration of the preform. Ceramic composites can be used for a wide range of applications: diesel and turbine engines, heat exchangers, turbines and missile nozzles. With regard to the manufacture of advanced gas-turbine engines, which would be lighter, more reliable and less bulky than traditional land engines, ceramic-ceramic composites could be used for high-load components, such as the turbine combustion chamber and regenerators, which would require no cooling, thus reducing the engine-specific fuel consumption, weight and overall dimensions, while improving its performances by increasing the engine operating temperature. (Ingeniers de l'Automobile (in French), November-December 1983, pp. 77-78.)

Ceramic for more durable cutting tools

The Department of Materials and Machining Technology of the Technical University of Lulea in Sweden is developing a new ceramic that could replace previous materials of machine steel for cutting tools. Quartz sand and air are treated chemically to form a powder with a grain size of 1/1000 mm with a silicon nitride base. This is treated with metal oxides and then the material is cold-pressed into a solid, after which it is enclosed in glass under a vacuum. The material is then placed in a hot isostatic press and sintered at 1600°C under a pressure of 200 MPa (2,000 atm). The ceramic is solid and free of pores. So far, the ceramic is relatively sensitive to blows and basic studies of the grain-boundary phases of the ceramics are being carried out. The new material has proven to be highly resistant to wear, high temperatures and thermal shock. The materials most comparable to the Lulea ceramic are hard metals (possibly coated), oxide ceramics, cubic boron nitride and industrial diamonds. (NY TEKNIK (in Swedish), 15 December 1983, p. 27.)

Bioglass: a ceramic for surgical implants

A new material called Bioglass has been developed by Larry Hench and a team of researchers at the Bioglass Research Centre at the University of Florida at Gainesville. The material forms a close bond with soft tissue and bone. Essentially the composition of this material is an inert soda-lime glass. Silicon dioxide accounts for 45 per cent by weight, with sodium oxide, calcium oxide and phosphorus pentoxide making up the remaining ingredients. The material becomes a ceramic when crystallized. The material was develcped by Hench in 1969 and, with the help of $2.5 million in government grants, he and a team at the Centre have identified the mechanism of the bond and developed applications for the material. Since Bioglass, like most ceramics, lacks strength when stretched or bent, research was directed toward applications where tensile strength is not of particular importance. "One of the most promising is making replacement bones for the inner ear. Operations to replace the malleus (hammer) bone are fairly routine, but bones made from metal or rubber form scar tissue sooner or later. This dampens the bone's motion, and gradually the patient loses the ability to hear high frequencies." In March, clinical trials were commenced with ear bones made from Bioglass. The bond that forms is a thin collagen fibre bond, as in nature. The team also started replacing roots of teeth with implants made from this material. "The idea is to prevent the deterioration in the jawbone that normally follows when a lot of teeth are extracted. Such deterioration eventually makes it impossible to wear dentures." The trials were carried out on five people, and so far with promising results, although it is too soon to speak about long-term results. "Perhaps the most exciting application for the material will be in replacement hip joints. Conventional replacements last for about ten years (although some fail much sooner) and are a once-in-a-lifetime operation. If they could be made to last longer, they could be given to much younger people .... But the everlasting hip joint is still a few years off." (Extracted from Michael Cross, "Ceramics bring long-lasting cures", New Scientist, 26 July 1984, p. 26.)

New Processes

New process for structural ceramics developed at Rutgers University

The Center for Ceramics Research at Rutgers University, New Jersey, has developed a process to produce structural ceramics that are 15 times stronger and more adaptable than most high-grade ceramics. The process involves transformation toughening, whereby a mixture of aluminium oxide and zirconium dioxide powders is pressed together at very high temperatures, reducing the size of the ceramic powders to under 1 micron. An organic dispersant is used to facilitate pouring the powder-water mixture into a mould for casting. The new ceramics have a fracture strength of 125,000 psi, in comparison with 5,000 psi to 10,000 psi for high-grade porcelain. ("New process makes ultrastrong ceramics", Chemical and Engineering News, v. 62, no. 16, 16 April 1984, p. 25.)

Use of ceramics for coke process

Krupp Koppers of the Federal Republic of Germany has developed a new process for preheating coal charges for coke ovens that is based on contact drying and heat conductions. Heat is transferred to the coal charge by solid heat-bearing ceramic spheres, with the combined advantages of being a large heat-exchange area and a high-density heat transfer agent. The heat capacity per unit volume is 1,000 greater than gases currently used in preheating plants. "In tests, at a spheres-to-coal mass ratio of 4:1 (volume ratio of about 1:1), the spheres cool down from about 400°C to 240°C. The coal, with a moisture content of 10 per cent, is dried in about six minutes and heated to about 200°C. ("New coke process uses ceramic spheres", Chemical and Engineering News, vol. 62, no. 18, p. 16.)

New ceramic-to-metal bonding technique

EG and G Inc., Idaho, the major contractor at the U.S. Department of Energy's Idaho National Engineering Laboratory in Idaho Falls, has developed a new process that may be applicable to heat exchangers, ceramic internal-combustion engines or other high-temperature applications. The new process first treats the metal substrate with various metal oxides that are deposited at 1 atm in a flowing gas environment of carbon dioxide and hydrogen. Nearly all of the oxygen is removed beforehand. Bonding with the ceramic material is rapidly carried out at around 2000°F. Conventional processes usually involve heating the metal and ceramic without the oxide layer in a lengthy process, causing undesirable oxides and bubbles to form in the ceramic. ("A ceramic-to-metal bonding technique has been developed at EG and G Idaho", Chemical Engineering, 2 April 1984, p. 19.)

New technology for thin, complex ceramics

Battelle Memorial Institute's Columbus, Ohio Division is developing a new manufacturing technology for producing thin, complex ceramics. Metal organic polymers are added to a conventional ceramic powder base. The polymers bind the powder together during extrusion, forming uniform, thin shapes. The ceramics can withstand severe environments such as high temperatures, wear, erosion, corrosion and creep fatigue. Possible uses include heat exchanges, batteries, combustors and catalyst carriers. ("Battelle is developing stress-tolerant ceramics", Chemical Week, 14 March 1984, p. 46.)

New process to prepare clay

Henderson Clay Products of the United States has installed a clay-preparation system at its plant in Marshall, Texas. This system prevents wet clay from stopping up, thereby improving production. The new system creates little dust and practically no noise. The system begins with a series of four hoppers at the feed end, three of which hold the clay and the other contains brick bats pre-sized in a jaw crusher for grog. All of the plant's requirements are produced in an 8-hour shift, yielding 40 tph of ground materials and requiring only two workers. Most of the clay can be prepared without drying, thereby lowering fuel. The colour-control problem is solved by better mixing. (Brick and Clay Record, May 1984, pp. 30-31.)

Spray dryers to convert slurry into powder

APV Anhydro Inc. uses a single-step, continuous, suspended particle, spray-drying process that converts nearly any pumpable solution, slurry, emulsion, suspension or paste in a free-flowing, homogeneous powder in a few seconds. A suction fan draws hot air through a distributor located at the top of the chamber at the centerline. The heated air supplies the necessary heat for evaporation, which takes place almost instantaneously due to the large liquid surface created by atomizing ceramic slurry into fine droplets. (Ceramic Industry, May 1984, pp. 26-29.)

Process to produce high-quality tile bodies

A dry mixing/pelletizing and vibrating fluid bed drying/cooling combination is used by the Jeffrey Manufacturing Division of Dresser Industries, Inc., United States, to make high-quality tile bodies. High-intensity dry mixers now available are capable of producing a homogeneous product, saving up to 70 per cent in energy. It is possible to obtain pellet agglomeration of the fine material by adding between 12 and 14 per cent water during the mixing process. The low moisture, pelletized clay body can be thermally dried in a vibrating fluid bed dryer to the required 6 to 7 per cent moisture content for tile-pressing. An efficient thermal processor is created as a result of the intimate contact between the material and the air stream of the fluid bed as well as the positive conveying of a vibratory conveyor. By combining a low-fluidizing velocity and mechanical vibration, materials that are difficult to fluidize can be processed. The vibrating fluid bed dryer can serve the processing needs of specific materials by controlling such process variables as speed, bed depth, drying time, air velocity and temperature. Even variations in the consistency and/or particle size of the clay body can be accommodated. The dryer/cooler units can reduce capital equipment costs of clay-body preparation and energy costs due to the 12 to 14 per cent content of moisture in the vibrating fluid bed dryer. (Ceramic Industry, May 1984, pp. 34-35.)

Process for producing sialon ceramics that withstand high temperatures

The National Institute for Research in Inorganic Materials of the Science and Technology Agency of Japan has developed a new technology for producing sialon ceramics that can withstand temperatures over 1200°C, which could have applications in ceramic automotive engines and machine tools. Sialon is a compound of silicon, aluminium, oxygen and nitrogen. In general, sintering raw material for ceramics at a high temperature requires an agent. However, when the raw powder has a diameter of 0.5 microns or less, sintering can be accomplished without an agent. Sintering can also be done at comparatively low temperature from 1600°C to 1650°C without an agent if the sialon is made into an ultrafine powder. The Institute has succeeded in making an ultrafine pulverization: particles as small as 0.3 microns in diameter were prepared with virtually no impurities.

The Institute first made alcohol compounds of both the aluminium and the silicon, and by hydrolysing then formed a uniform mixture of very fine aluminium oxide (alumina) and silicon oxide (silica) particles with a diameter under 0.02 microns. As a result of mixing carbon particles of less than 0.05 microns into this and heating it to a temperature between 400°C and 500°C in a nitrogen atmosphere, they obtained a fine sialon powder of high purity. It is generally known that if the powdered raw material's diameter is under 0.5 microns, sintering can be down without an agent. Even if the particle diameters grow during sintering, it is not enough to affect the strength adversely if the powder initially is fine enough. Having this ultrafine power of around 0.2 microns, any lessening of strength at high temperatures is prevented. Sialon is drawing attention as a new material in which one part of oxygen replaces part of the nitrogen in the silicon nitride, and one part of aluminium replaces part of the silica. It has been possible to obtain material with only about the same strength characteristics of silicon carbine with the usual production methods. The reason is that current production methods do the sintering by adding aluminium nitride and alumina to silicon nitride powder as the agents, so that the purity cannot rise any higher than 98.5 per cent. Also, during sintering the particles making up the ceramic grow to between 5 and 10 microns in diameter. In general, the larger the diameter of the particles forming the ceramic, the weaker the mechanical strength. The use of such agents as magnesium oxide or yttria to sinter the silicon nitride powder stay vitrified as low melting-point compounds. When such substances are again exposed to high temperatures, the ceramic easily breaks down at such zones. Also, the strength is decreased if the raw silicon nitride powder particles grow large in the sintering process. (Nikkei Sangyo Shimbun (in Japanese), 27 March 1984, p. 18. Copyright 1984 by Nihon Keizai Shimbunsha and The Japan Economic Journal, 17 April 1984, p. 17.)

Nitrided pressureless sintering and rate-controlled extraction

In a project to develop high-temperature ceramics for fuel engines, the Swedish Silicate Research Institute (SSFI) is using two new processing techniques. One involves sintering, i.e. densifying the material during firing of silicon nitride, and the other removes organic binding agents after injection moulding. Nitrided pressureless sintering (NPS) involves a combination of nitrided silicon and pressureless sintering. Silicon is milled with the sintering agent in a matrix of silicon nitride. A ceramic body is then formed with the powder mixture and the silicon is nitrided to form silicon nitride at a temperature between 1300°C and 1400°C. In this step, a large part of the pore system is filled in, but the surface geometry of the ceramic body remains substantially unchanged. In final sintering at 1800°C, the material is completely densified. Because the nitride step fills in the pores, linear shrinkage amounts to only between 8 and 9 per cent, as compared with around 15 to 20 per cent during normal firing. The method also seems to be an improvement on an earlier approach used by Ford and Fiat. Their sintered reaction bonded silicon nitride method was also based on silicon and a sintering agent, but the nitride step was very slow, taking several days, compared to a few hours for the NPS technique. The secnd new technique is called rate-controlled extraction (RCE). This is an improvement over earlier techniques for shaping construction ceramics. One such method is injection moulding, whereby a large quantity of ceramic powder in a plastic matrix is formed by injecting it into a mould. The most critical element is then to remove the organic binding agent. With the binding agent accounting for between 30 and 40 per cent by volume, its removal without causing defects is essential. Because of its elastic nature, ceramic material is less tolerant of defects than construction materials that can be distorted plastically. The result is generally poor durability. With the new technique, the component is placed on a kiln and its weight and thus the weight of the organic binding agents is registered continuously. Information on the time, temperature and weight are continuously monitored by a microcomputer to control the speed with which the binding agent is removed. Thus, throughout the process, rapid but precisely-controlled binder removal is maintained. (Kemisk Tidskrift (in Swedish), January 1984, pp. 37-40.)

Super-micronization of ceramics

By the use of activated conditions of hydrogen arc plasma to burn materials under a hydrogenous atmosphere, super-micro particles below 0.1 micron have been obtained from the burning gas through a process developed by the Metal Materials Research Institute of the Science and Technology Agency of Japan. The super-micronization technology is relatively simple: an arc discharge is made under a hydro-nitrogenous atmosphere with the pressure reduced by a vacuum, characteristically with low cost and without contamination of the ceramic surface. Greater quantities of ceramics can be manufactured with the chemical treatment method. Super-micronized ceramics have good prospects for a wider range of application as materials for electronics, such as magnetic tapes, integrated-circuit basic panels, vibrators, etc., and as artificial bones and whetstones. (Nikkan Kogyo Shimbun (in Japanese), 7 October 1983, copyright 1984 by Nikkan Kogyo Shimbunsha.)

Market Trends

Potential for new ceramics

"... new ceramics may greatly affect present-day industry, society, and even culture and may transform our daily lives. That is the importance of the role and social impact of the new materials known as new ceramics."

"Given that new ceramics will change industry and society so much, it is to be expected that companies will see investment opportunities in this field, and in fact the new ceramics industry in Japan right now is estimated to have over 200 manufacturers, including those still working only in research and development."

Impact of new ceramics on various fields

Materials industry	New ceramics are being actively developed for higher added value and as a new source of income. Many existing products and materials are being supplanted by new ceramics. There is an income and profit gap between companies which are late in developing new ceramics and those which are not.
Energy industry	New energy devices such as high efficiency gas turbine engines using new ceramics are being refined.
Automobile industry	A fuel economy revolution is taking place with light composite materials reinforced with carbon or boron fibers and with development of ceramic engines. In adopting new ceramics, automobile companies must invest in new equipment and remodel production lines. Automakers are also seeking sources of supply abroad.
Semiconductor industry	Following silicon, GaAs semiconductors have appeared, as will Josephson elements in a post-IC era. The scale of IC integration is accelerating.

Telecommunications and information equipment industry	As optical fibers become more effective and less costly, they will come to replace coaxial cables. Optical fibers will be used more widely in the fields of personal media, cable TV, pushbutton phones, and home facsimiles.
Precision machinery industry	Since improved processing control is needed for acceptance of new ceramics in various industries, the precision machinery industry will grow.
Aerospace industry	The development of heat-resistant tiles and other new ceramics has made possible the reuse of rockets. Factories in space will be capable of creating new ceramics of high purity.
Resource consumption	Using ceramics for the principal parts of engines will make it possible to reduce fuel consumption by 30 per cent and reduce nationwide oil fuel consumption by 10 per cent. New ceramics, made from abundant resources will come to replace expensive rare metals in heat-resistant materials.
Equipment investment	The new ceramics industry, at least in the beginning, will produce specialized rather than general-purpose materials. It will be characterized by multikind small-lot production of products with high added value. Thus equipment needs for manufacturing each new ceramics product will be small.
National security	Since new ceramics are a basis for many advanced industries (electronics, aerospace, optical telecommunications, energy, etc.), not to have independent technological resources in this field would be hazardous for national security. The development of new ceramics is necessary to maintain bargaining power with advanced countries.
Culture	New ceramics will make the structure of production in Japan more sparing of energy and resources, and a desire for energy and resource conservation will take hold in the public's sense of values. Demand will shift from limited resources like metals to abundant materials like new ceramics, and people will turn to these materials more and more.

Welfare	Alumina, sapphire, and other new ceramics will come into use as materials for implantation in the body, and medical technology will progress. Since the final stage of processing new ceramics is indoor work and not physically demeaning, the handicapped will have new opportunities for employment.

(Extracted from Hidehiro Kimura, "The new ceramics industry in Japan: present state and future prospects", LTCB Research, no. 68, special issue (September/October 1983),pp. 5-6. Reprinted by permission of the publisher, The Long-Term Credit Bank of Japan, Ltd., Tokyo.)

Three ways to participate

"The companies which have entered the field of new ceramics can be classified by motive into the following three broad categories ....

(1) Diversification by materials manufacturers to apply existing technology to achieve higher added value and create more profitable products than their slow-selling current ones. This is the motive for many companies in the textile, petrochemical, and metal industries. For example, the steel industry has over the years accumulated much experience in development technology for refractory and coal-based chemicals, as well as technology for the testing of materials, and with annual steel production levelling off at 100 million tons a year, the industry is branching out into new ceramics. But, as with electric wire manufacturers, there is also a form of participation in which a company makes a new ceramics product (like optical fibers) which competes with its own traditional product (copper electrical wire), (2) Upgrading of an existing technology, in which research and development of the properties of products a company has long been producing, such as porcelain, glass, or refractories, makes it possible to give them new functions and properties and allows a changeover to high added-value production. This is how companies in the "old" ceramics industry, like the Kyocera Corporation, are participating in the new ceramics industry ..., and (3) Participation by processing and assembling industries, in which the users of materials are led by necessity to develop new materials on their own. Examples of this are found in the electrical equipment industry, where Toshiba Corporation is strengthening its materials research division and developing new ceramics, and in the automobile industry, where automakers are engaged in the joint development of ceramic engines with materials manufacturers ...." (Ibid., pp. 5-7.)

Tomorrow's producers

"The new ceramics business today is like a marathon with a large number of entrants. The race is not yet half over, and all the runners are bunched together in a pack. In electroceramics, an especially high-skilled field, and in the development of sensors, smaller companies and venture businesses may emerge as strong runners, but in the engineering ceramics division, because of the nature of the new ceramics business, large existing companies have the advantage .... Automakers who conduct joint studies with ceramics makers have a big head start in ceramic engines because they (and other specialized manufacturers) already dominate the market for gasoline, diesel and other engines. It is hard to conceive of them contracting out the work (to materials manufacturers, for instance) for engines, which are the essential part of any automobile, and because they are putting a great deal of effort into research and development of ceramic engines as the next generation of engines. But it is quite possible that materials manufacturers and other entrants to the new ceramics industry will take on the role of auto parts manufacturers, in business tie-ups or joint development projects with automakers. This is because there are no advantages of scale to be realized by producing only 1,000-2,000 of each ceramic engine part per month; indeed, at this volume, mass production would be inefficient. Also, cement manufacturers have the advantage of experience in sintering and other technology relating to new ceramics, but having only just begun a serious research and development effort, they are off to a late start in the ceramics marathon."

"To make up for lost time, latecomers to the new ceramics field will have to seek technology from or form business tie-ups with foreign manufacturers or more advanced domestic manufacturers."

"New ceramics are obviously of great importance in national strategy, for this field of advanced technology also forms a base for many other high-tech industries. Because of the high degree and depth of technology required, developments in this field are a focus of rivalry among the industrially advanced countries. The technology will eventually be transferred to other countries, however, and it is possible that NICS will come from behind to take the lead. Electroceramics are one possible example. Electroceramics are already in the stage of mass production, and unit costs are low; the 300 or so condensors used in a video tape recorder, for example, cost about 1.3-2.0 yen each. Since 30-40 per cent of the cost of such products is labor, products made in developing countries, where wages are relatively low, will have a price advantage that will make them internationally competitive. In new ceramics, as in the steel industry, near-developed countries may in the future take the lead in general-purpose products, while Japan and other countries advanced in new ceramics will be forced to shift their production to higher-grade, higher added-value products."

"Japan, therefore, may find it necessary to cooperate in various ways internationally: on a private basis through international business tie-ups, joint development projects or local production, and on a government basis by playing a leading role in international technical cooperation and in setting standards for evaluating the quality of new ceramics. It should be pointed out that international cooperation is just as essential as competition for the development of new ceramics technology and the new ceramics industry." (Ibid., pp. 15-16).

Market forecast for Japan

"Electroceramics, which make up 70 per cent of the demand for new ceramics, will constitute an approximately 540 billion yen market in 1990. In addition to the demand for IC packages, various types of sensors will come into wide use, so that demand for electroceramics will grow at about 10-15 per cent a year."

"The biggest factor in future demand for new ceramics is automobiles, and in this area, one of two things may happen: (1) practical ceramic diesel engines will be developed and come to make up about half of all diesel engines in use, or (2) the structure of engines will remain about the same as it is today, but with almost all replaceable parts made of ceramics. In the first case, since the market for engine parts (the total for pistons, cylinders, etc. but excluding radiators and other parts which will no longer be needed because of the changeover to ceramics) is estimated at 840 billion yen in 1990, a diesel conversion rate of 50 per cent would mean creation of a new 420 billion yen market. (Assuming that all engines will have been replaced by ceramic engines by 1990, the market for these engine parts may be estimated as follows. (1) If about Y710 billion in total engine production in 1979 increases at an annual rate of about 3 per cent, engine production will reach Y980 billion by 1990. (2) With the advent of ceramic engines, some parts like radiators will become immaterial. Production of such engine parts in 1979 was about Y100 billion, accounting for 14 per cent of total engine parts production. In this context about Y140 billion worth of engine parts will be eliminated in 1990. (3) Accordingly, Y980 billion minus Y140 billion will be the market size of diesel ceramics engine parts in 1990.) In the second case, the value of ceramics-replaceable parts produced in 1990 is expected to be about 280 billion yen (about 30 per cent of the approximately 980 billion yen value of all engine parts produced in 1990), creating a sizeable market. Apart from these two possibilities, considerable strides are expected in research and development in the conversion to ceramics of gas turbine engines and other engines having a different structure from those of today, but for 1990 the above two goals are considered the most realistic."

"Bioceramics will form a new and growing demand. Bioceramics began to receive a great deal of attention about ten years ago as material for prosthetic implants to repair injured organs or tissues. New ceramics are now used for artifical teeth roots, artificial hip joints, artificial bones, and fixing screws implanted in broken bones. The market for bioceramics will grow steadily. If about 20 per cent of all extracted teeth are replaced with artificial teeth with ceramic roots, this alone would be potentially a 100 billion yen market. Bioceramic materials include alumina, apatite hydra and crystal glass, but recently bioceramics such as high-purity beta-crystalline calcium phosphate and calcium carbonate have been developed which are stronger and function better than conventional ceramics. The areas of application for bioceramics will expand considerably. Mitsubishi Mining and Cement Co. Ltd. has been doing research in artificial bones and is ready to put its results to practical use. Bioceramics can be expected to constitute about a 100 billion yen market in 1990."

"There will also be considerable new demand for new ceramics for fuel casings, control rods, and moderators in nuclear power plants, structural material (walls of vacuum chambers) in fusion reactors, and other applications for various ocean development equipment, where corrosion resistance is a must, and for electric vehicles. It is thought that the overall market for new ceramics in 1990 will total 1.2-1.3 trillion yen."

Estimated market size of new ceramics

	1981	1990	Annual growth rate (%) (in 100 millions of yen)
Electronic ceramics	1,900	5,400	12.3
Engineering ceramics (engine parts except spark plugs)	0	1/ 4,200 2/ 2,800	- -
Bioceramics	10	1,000	29.2
Total *	3,000	1/ 12,700 2/ 11,300	17.4 15.9

1/ A case in which a ceramic diesel engine would be put on the market, and installed in half of the vehicles produced.

2/ A case in which engineering ceramics would be used as widely as possible with the current engine structure unchanged.

* Total includes ceramics for miscellaneous uses.

(*Ibid.*, pp. 5-6).

Japanese consumption

"... according to a survey (conducted by the Fine Ceramics Association, Shinroku Saito, president, 172 member companies) of manufacturers and users of new ceramics-related raw materials and parts, manufacturing equipment, and testing equipment, the growth in this field has been about 10 per cent per year: from 290.2 billion yen in 1981 to 308.6 billion yen (est.) in 1982 and 345.8 billion (est.) in 1983."

Production of new ceramics in Japan
(in billions of yen)

Application	1981	1982	1983
Mechanical	61.4	62.4	74.0
Heat	9.49	11.2	13.5
Electromagnetic	197.0	211.9	230.4
Optical	1.72	2.94	4.23
Chemical and biochemical	16.2	15.6	18.6
Others	4.39	4.57	5.11
Total	290.2	308.6	345.8

Note: The figures are actual for 1981, estimates for 1982 and 1983.
Source: Fine Ceramics Association.

(*Ibid.*, p. 2)

Good prospects for lower prices

"... the natural resources from which existing materials are made are becoming depleted. The engines of a jumbo jet, for example, contain 1 to 2 tons of cobalt in their heat-resistant alloys. But cobalt, as well as chrome for corrosion- and heat-resistant alloys and tungsten for super-hard alloys, is not very plentiful; it is available, at high prices, only from certain countries like the Republic of South Africa and Zaire, and a stable supply is not assured. However, the raw materials for new ceramics, alumina and silica for example, exist in large quantities all over the world, so their supply is both plentiful and stable. Despite the high growth expected for new ceramics, the market is still small. This is because, when we consider the life cycle for materials, new ceramics are only in the early stages of development and production. It will be some years to reach mass production, which will lead to lower prices, increased demand, and more mass production. In this connection, carbon fiber, a material which has shown rapid growth and is used in the space shuttle and the B767, cost 300,000 yen per kilogram a little more than ten years ago; today it costs only 10,000 yen per kilogram, and the price is expected to drop further." (*Ibid.*, p. 2)

Advantages in auto engines

"New ceramics have the following four advantages, which we will illustrate by considering ceramic engines: (1) They increase fuel efficiency (by allowing combustion at temperatures too hot for metals), (2) Engines can therefore be built which require no cooling system (and which, without radiator, pump or fan, are lighter, smaller and cheaper), (3) Unlike expensive heat-resistant rare metals, the raw materials for ceramics exist in unlimited supply, implying lower cost and resource conservation, (4) Since the specific gravity of ceramics is about 3-4, and no oil or cooling water are required, a ceramic engine (although this weight loss is offset by the need at present for adding a "turbocompound", a device which recovers exhaust heat and revolves on the crankshaft)."

"A typical light automobile engine today weighs about 100 kg, has an efficiency rate of 25 per cent, a turbine intake temperature of about 1000°C, a a heat exchanger intake temperature of about 700°C. A ceramic engine weighs about two-thirds of this, has an efficiency rate of 46-50 per cent, a turbine intake temperature of 1370-1400°C, and a heat exchanger intake temperature of about 1100°C. A ceramic engine requires less energy and material to build and has a lower material consumption density."

"Here is a specific estimate of how the nation would be affected by the general use of ceramic engines:

(1) If fuel efficiency is increased by making the main engine parts of ceramics, then assuming that fuel efficiency increases 30 per cent due to ceramic engines, the transport sector, which accounted for 34 per cent of all the oil consumed in Japan in 1982, would consume only 30 x 34 per cent = 10.2 per cent of the total, and oil fuel consumption in the nation as a whole would decline by about 10 per cent.

(2) An automobile engine requires 1-1.5 kg of high-grade heat-resistant alloys of cobalt, nickel, and chrome. If ceramics can replace half of these alloys, the total amount saved would be 0.75 kg x 13 million vehicles (assumed as the number of cars and trucks produced in Japan) = 9,750 tons. Of this amount, 260-300 tons of cobalt would be saved, an amount which represents 10 per cent of Japan's cobalt consumption in 1976 and a 70 per cent cut in the amount of cobalt used in heat-resistant alloys (430 tons in 1976).

(3) Consumers would benefit from the use of new ceramics and new lightweight materials in automobiles, for this would raise the fuel efficiency of a typical car from 9.0 to 12.0 km/liter, making a difference of about 5,000 yen a month in gasoline costs. This works out to about 60,000 yen a year, which is no negligible sum for a fmaily budget (see note)."

"Note: Average distance travelled per month by a small car (Ministry of Transportation data): 1,089 km. Distance travelled per liter of fuel (Automobile Industry Association figures): 9.0 km in fiscal 1975, 12.0 km in fiscal 1980. Price of gasoline per liter (consumer price as of the end of January 1982): 165 yen. Making the above assumptions, the amount of money saved comes to (1,089 km ÷ 9.0 km-1,089 km ÷ 12.0 km) x 165 yen = 4,991.25 yen, or 4,991.25 yen x 12 = about 60,000 yen per year per small car."

'The full use of new ceramics in automobiles can confer the great economic benefits we have described above." (Ibid., pp. 4-5)

New applications: electronics, insulating and structural materials

"At present, new ceramics applications may be divided into two broad categories: electronics and insulating and structural material. Electroceramics, which account for about 70 per cent of the demand for new ceramics, are used in condensors, IC packages, thermistors, and baristors; some 230-240 billion yen worth of them were expected to be produced in 1983. In the other broad category, heat-resistant and structural ceramics, are high-temperature gas turbines, nuclear reactors, and MHD (Magneto-Hydro Dynamic) power generation; this field is in the development stage, and practical applications cannot be expected until the 1990s.

The 30 per cent of today's new ceramics market which excludes electroceramics includes ceramics for magnetic materials, super-hard materials (bearings, tool bites), optical materials (optical fiber, transparent electrodes), and bioceramics (artifical teeth)." (Ibid., pp. 2-3)

Processing objectives

"One consequence of the high melting point of ceramics is that they must generally be fabricated from powders rather than melts. Changes to the ceramics powders during sintering or firing ar therefore important. In the most idealized form, solid state sintering, the powder consists of individual crystals which remain solid throughout the heat treatment. The system is heated to temperatures where diffusion of the atoms in the solid state can occur; atom movements can then reduce the surface energy of the system either by densification - movement of atoms from the grain boundary region to the solid/gas interface - or by coarsening - movement of atoms between different regions on the solid/gas interface. Densification reduces the distance between particle centres, so the component shrinks up to 20 per cent, which removes porosity. The coarsening process, in contrast, wastes the surface energy which provides the driving force for densification without changing the porosity."

"These processes are speeded up by higher fabrication temperature (faster atom diffusion) and by fine uniform particles (shorter diffusion distance, less material to move for a given shrinkage) of sub-micrometre size. Densification is enhanced if pressure is applied to the system during heating to increase the driving force for shrinkage and pore elimination. Coarsening is reduced if the powder particles are all of similar size. The firing can reach temperatures of 1650°C for aluminium oxide; 1700°C for zirconium oxide and 2050°C for sinterable silicon carbides."

"Poor densification and bad mechanical properties are to be avoided. A common difficulty with silicon nitride and silicon carbide, for example, is that coarsening is relatively favoured with the result that simple heat treatment of powders is ineffective. One solution is to use an additive which yields a liquid phase between the grains at the firing temperature; this acts as a rapid diffusion path for material from the grain boundary and densification can occur, particularly if assisted by pressure. Magnesium oxide (in concentrations of 5 per cent by weight) acts this way in the sintering of silicon nitride powders. The difficulty then lies in removing the additive from between the grains to avoid creep in use. Possible solutions are to crystallize the boundary phase or to make it form a solid solution with the grains; both approaches are being actively pursued in the case of the sialons, the family of new silicon nitride related materials (containing Si-Al-O-N and other elements) developed by Ken Jack and his colleagues at the University of Newcastle."

"An attractive alternative way to aid densification is to use an additive which acts without forming a liquid phase at the boundaries; trace additions of magnesium oxide work in this way for aluminium oxide, a feature discovered by Bob Coble when at General Electric, Schenectady, and now routinely used to make envelopes for sodium street lamps. The additive/host system is effective for many reasons (magnesium oxide seems to raise the lattice diffusion rate and to suppress the surface diffusion rate), so this has been tried with many ceramics."

"Fine powders cause another problem as grain sizes fall below 1 micrometre. The powder becomes more difficult to handle and the particles tend to form agglomerates. The powder than acts, to all intents and purposes, in the same way as a coarse powder with a particle size corresponding to that of the agglomerate. Bill Rhodes at the GTE Laboratories has shown the potential merit of fine powders by demonstrating that zirconium oxide can be sintered to full density at 1100°C in place of the more normal 1700°C if a genuine particle size of 30 nanometres can be achieved. The precautions needed to avoid agglomerate formation in powders of such size are extremely demanding."

"A final problem is that conventional firing can yield results only as uniform as the quality of the powder compact. If severe variations in packing density occur in the compact, then corresponding inhomogeneities and faults will occur in the finished product. Two general approaches can then be adopted. In the first, recognizing that some faults will occur, a final hot pressing step can be added to the processing sequence following a preliminary firing."

"In hot isostatic pressing, partly sintered parts of reasonable density, that is, where porosity occurs as isolated voids but where occasional large voids occur, are heated under an imposed gas pressure to remove the last trace of porosity. The development of sophisticated non-destructive tests to show that all porosity has been removed is important to this approach and is the subject of much research."

"A second approach sets out with the objective of making the ideal compact: an even, well-packed structure of uniform, spherical, sub-micrometre particles. This methods requires meticulous powder preparation by controlled nucleation and growth from solution, followed by structural assembly achieved by carefully balancing interparticle forces within the solution; it has been pioneered by Kent Bowen and colleagues at MIT and the results can be spectacular."

"The present objectives of processing research are clear because we know precisely what ceramic components are needed. The target is one of achieving convenient, practical and reliable procedures capable of providing these components. The centre of activity has, if anything, moved into the prefiring stage where methods of preparing and handling powders are being developed to reduce the maximum size of faults within the material. At present, it appears that before the ideal compact arrives, ceramics factories can make very substantial improvements by imposing clean rooms and other refined production methods familiar in semiconductor work. Such a development is very much at the core of research programmes where flaw sizes of 10 micrometres or less are sought." (Extracted from Richard Brook and Frank Riley, "Density means toughness", New Scientist, 26 January 1983, pp. 14-16.

The market in heat engines

"The main application for ceramics lying at the end of the many national development programmes is that of the heat engine, and there is an international race to fit ceramic components into such engines. A wide range of gas turbine and diesel engine prototypes has been constructed, and run, with ceramic hot-zone components. Governments (notably the US, Japanese and German) are budgeting large sums to finance research in this area. One reason for this level of activity is that the market value for ceramics in engines is predicted to be large. Japanese estimates suggest that by 1990 some £750 million of ceramic components annually will go into cars, and £675 million into other vehicles." (Ibid.,p. 16.)

New approaches to the design of components

"There are two complementary avenues to make strong components. The first is to reduce the size of fault found in the ceramic by improving the processing; the second is to increase with toughening mechanisms the energy required to extend a crack in the material."

"The latter approach draws attention to the clear distinction between ductile metals and brittle ceramics, namely that the metals require 100,000 times more energy before a crack will extend. An example of toughening is fibre reinforced composites. A second example is transformation toughening of ceramics which has been extensively developed by Ron Garvie (CSIRO, Australia), Nils Claussen (Max Planck, Stuttgart), Fred Lange (Rockwell, California) and their colleagues. Transformation toughening doubles the fracture toughness of a ceramic such as aluminium oxide (and hence, for a given crack size, the strength) if 15 volume per cent of fine (about 0.3 micrometres) inclusions are added to the material."

"Zirconium oxide undergoes a crystallographic phase transformation on cooling from high temperature (above 1200°C), in which the change from tetragonal to monoclinic crystal symmetry is accompanied by an expansion of the crystal lattice. If fine zirconium oxide particles are constrained within a matrix material such as aluminium oxide, the transformation is prevented as the material cools from the fabrication temperature (about 1650°C), with the result that tetragonal particles stay at room temperature."

"One explanation for the extra toughness is that these particles, when placed in the locally enhanced tensile stress field at the tip of an advancing crack, are freed from the constraint of the matrix and change to the larger-volume monoclinic form. As a crack advances, the local stress field advances with it, and the constraint of the matrix is reimposed on transformed particles. The particles are, however, unable to retransform, owing to the structural complexity of the transformed state and the resulting strains add to the energy required for fracture, G. Such toughening mechanisms are being studied by Tony Evans and his group at UC Berkeley, among others."

"Transformation toughened materials are known with bend strengths reaching 2 GPa (equivalent to high tensile engineering steels) and with projected strengths of 3 GPa. Significant increases in fracture toughness have also been achieved; values some three times greater than those of unmodified materials, have, for example, been obtained by Ron Stevens and colleagues at Leeds."

"Engineering components must have creep resistance at high temperature as well as mechanical strength. The material should sustain loads at high temperature without any progressive distortion. In particular, the material should not contain any phase that becomes liquid at high operating temperatures, so increasing creep by creating lubricated surfaces between the grains." (Ibid., pp. 13-14.)

Growing attention for ceramic whiskers

Ceramic whiskers are attracting more and more attention because, as compared with ceramic fibres, they are thinner, shorter, have greater fracture toughness, stiffness and maintain their physical properties at high temperatures. They are currently used less than ceramic fibres because they have not been on the market very long and companies have little experience with them. Whiskers made of silicon carbide are gaining attention: they have a diameter of about 0.5 metres, whereas a fibre of the same material ordinarily has a diameter of 10 metres or more. Ceramic whiskers can have a tensile strength of between 3 and 4 million psi at room temperature, whereas ceramic fibres have only .3 to .5 million psi. Ceramic whiskers range in length between 10 and 80 metres, whereas some fibres are measured in only centimetres. (Howard J. Sanders, "High-tech ceramics", Chemical and Engineering News, v. 62, no. 28, 9 July 1984, p. 35.)

News From Developing Countries

Development and quality control of ceramic materials in Brazil

Research in the field of ceramics began 50 years ago, with two institutions performing research, the Technological Research Institute (IPT) in São Paulo and the National Institute of Technology (INT) in Rio de Janeiro.

"Dr. Pérsio Souza Santos in São Paulo was the leader and the precursor of all systematic characterization of Brazilian clays and other raw materials for the ceramic industry. The methods were improved with time, and now, not only precise classification can be performed, but raw materials modifications and adaptations to new processing methods can be done in Sao Paulo and in several other places in Brazil. All those places have someone trained by Dr. Pérsio."

"In the mid-1970s, other research laboratories began to do research in ceramics. One of the main laboratories is at the Federal University of São Carlos, Department of Engineering Materials. "The research interests are towards high technology ceramics and glasses beginning with powder preparation, development of methods for powder processing characterization, sintering, and properties related with microstructure. Materials studied at the present time are: Alumina. Preparation of high surface area, sodium-free, and deagglomerated alumina, starting with controlled calcination. Methods to precisely characterize the various transition phases and their relation with atmosphere and forward processing. Flowability of powders, additives for grinding and pressing. Mechanisms of powder mold filling, Sialon. Preparation and sintering is beginning with clays of various compositions and mineralogy. Influence of several parameters over the reduction kinetics, powder processing, and sintering under controlled atmosphere. Densities after sintering of better than 95 per cent and with less than 1650°C temperature. Studies about sintering kinetics and mechanisms. Effect of additives, Electronic Ceramics. Dielectrics and ionic conductors. Production of barium titanate beginning with Brazilian raw materials. Production of β"-alumina powder, from controlled purity starting α-alumina precursors prepared in the lab, Ceramic Composites. Sialon-alumina, cordierite-mullite and cordierite-alumina composites were prepared and their thermal shock and mechanical properties measured. Some improvements in toughness could be obtained with controlled particle size, or large increases in the critical temperature for thermal shock, Phosphate Bonding in Refractories. High alumina mixes can be stored for more than a year without losing plasticity, with adequate addition of plasticizers and inhibitors. Chemical reactions involved are pointed out. Controlled pH phosphates are used in basic mixes, and the mechanical properties at room and high temperature tested, Glass-Ceramics. Kinetics of amorphous phase separation, crystal nucleation, and crystal growth in binary silicates and borates (Na_2O, Li_2O, BaO, PbO). Development of glass ceramics from natural minerals."

"Several industries also have laboratories that are mainly used for development and quality control of ceramic materials. "The refractory materials producers are very well equipped for sophisticated work, so they can guarantee their products. Characterization and processing of their raw materials are carefully performed, and high temperature properties measurement and electron microscopes are common capabilities. The sanitary ware industry is very well developed too; several papers published in Brazil in the monthly magazine Cerâmica come from developments obtained in raw materials or slip casting work done in their own labs."

"Currently several industries producing high technology ceramics are emerging. With them, the possibilities for interaction with research labs are much better, and some can reproduce products in high alumina with properties comparable to the best available. The research being done in São Carlos in alumina processing has transferred some of its achievements already to small production lines of lab ware, without purchasing any outside technology." (Extracted from José Roberto Casarini, "Current ceramic technological and scientific research in Brazil", American Ceramic Society Bulletin, vol. 62, no. 9 (1983), pp. 998-999).

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NEW CERAMICS

John B. Wachtman, Jr.* and Malcolm G. McLaren**

Introduction

A new era has opened in the manufacture and use of ceramics. Throughout the industrialized world advances in products and competition in performance, cost, and reliability are driving materials, including ceramics, to new levels of sophistication. The new ceramics have their roots in the past, of course. In many cases their promise was seen two decades ago and research has been underway for a long time. The flowering of new ceramics results from a confluence of research results, market conditions, and a world-wide attempt by many firms, aided by Governments in many cases, to stake out future positions in high-technology products.

The new ceramics go under several names. For example, in Japan they are called either "new ceramics" or "fine ceramics". In the United States of America they are frequently called "high-performance ceramics" or "advanced ceramics". In all cases the terms refer to a broad and diverse group of ceramic materials that are not easy to embrace in a simple definition. Their distinguishing features in general are a substantially higher level of performance, much more stringent requirements on composition control and processing, and a market value based on unique performance, which justify a much higher cost and higher value added per kilogram than is characteristic of traditional ceramics. Within this broad overall definition many families and sub-families of advanced ceramics exist and continue to grow and multiply in number and kind.

A market estimate for advanced ceramics

Comprehensive statistics on ceramics, especially advanced ceramics, are difficult to obtain. Conventional economic statistics concentrate on the older families of ceramics, such as building materials. Much of the activity on new ceramics is included in economic totals for organizations in other economic categories and can only be partially broken down, if at all. One can use surveys by various market research organizations as a rough guide. A broad overall feeling for the size of this market is provided by the estimate in table 1.

Table 1. World market for advanced ceramics
(in billions of $US)

	1980	1990	1995
Japan	1 900	6 500	9 000
United States	1 500	5 000	7 000
Other market economy countries	700	500	1 000
Total	4 100	12 000	17 000

Source: The estimates shown above were developed by H. Kent Bowen for the Committee on High Technology Ceramics in Japan and appeared in John B.Wachtman, Jr., "Ceramic fever: advanced ceramics in Japan," *Ceramic Industry*, Vol. 121, No. 6, (December 1983), p. 29.

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The estimates assume success for a limited range of ceramics for heat engines, but do not assume a full ceramic engine. Electronic ceramics and structural ceramics account for roughly equal shares of this market estimate. Other estimates vary widely, especially with regard to the timing of future growth. For example, Candice Stevens of the United States Department of Commerce estimates that the market for ceramic-based electronic components in the United States will be $19.7 billion in 1990, but is more conservative about the growth of structural ceramics, placing the greatest growth in this field after 1990. All that can be said with reasonable assurance is that the future market for advanced ceramics will be large, will have a high growth rate and offer good opportunities. This market prospect has attracted the attention of many aggressive firms, especially in Japan and the United States. The low estimate in table 1 for the probable future market in countries other than Japan and the United States reflects the concentration of the current activity on producing and using advanced ceramics in these two countries, plus the view that future growth will require mastering very difficult production technology while competing fiercely on price. There seems to be no inherent reason why firms in other countries could not take a larger share of this growing market, provided they can bring the technical and financial resources together in an organization that can deliver reliable products on time at a competitive price and simultaneously move with the developing technology. Joint ventures in new ceramics by firms in developing countries in conjunction with firms in developed countries appear very promising.

Advanced ceramics classified by function

New ceramics are generally used as parts in devices because they can perform some functions better than competing metals or polymers. Many of these applications rely on the special electromagnetic properties, sometimes in combination, of ceramics: their relative chemical inertness, hardness and strength, and their ability to withstand high temperature capabilities. A systematic classification is provided in table 2.

The first classification by electric functions is broad and requires discussion in terms of more detailed categories. Electrical insulation materials are descendants of traditional electrical porcelains in a sense, but the properties required and the size and complexity of the integrated ceramic parts make them a new family of materials. Aluminium oxide, ranging in purity from 90 per cent to 99.5 per cent, depending on the application, is the dominant ceramic electrical insulator. Refinement of the tape-casting process in the early 1970s made it possible to produce unfired tapes with sufficient strength for handling, including punching of holes, inking, stacking, etc. When fired these tapes produce ceramics typically 50 microns to 100 microns thick with bending strength values greater than 275 megapascals (MPa). These ceramics compete with polymers and coated metals as supports for electronic chips and dominate in applications where high-heat dissipation and high hermeticity are required. This technology is highly developed and includes multi-layered substrates composed of more than 30 layers, with tens of thousands of interconnections by thin metal layers applied as inks and fired with the ceramic. Excellent as alumina is for this application, alternate materials are being studied in an attempt to lower the dielectric constant to permit higher frequency operation and a better match for the thermal expansion of silicon. Multiphase ceramics in the aluminium oxide-silicon dioxide-magnesium oxide family may be the next generation of ceramics. Silicon nitride may eventually be the third generation.

This situation illustrates both the opportunity and the difficulty for a developing nation to produce one of the new ceramics and gain a market share. The opportunity for ceramic substrates for electronic chips appears to be very good. The immense growth of industrial and consumer applications of micro-electronics

Table 2. Classification of high-technology ceramics by function

Electric functions	Insulation materials (Al_2O_3, BeO, MgO)	IC circuit substrate, package, wiring substrate, resistor substrate, electronics interconnection substrate	
	Ferroelectrics materials ($BaTiO_3$, $SrTiO_3$)	Ceramic capacitor	
	Piezoelectric materials (PZT)	Vibrator, oscillator, filter, etc.	
		Transducer, ultrasonic humidifier, piezoelectric spark generator, etc.	
	Semiconductor materials ($BaTiO_3$, SiC, ZnO-Bi_2O_3, V_2O_5 and other transition metal oxides)	NTC thermistor:	temperature sensor, temperature compensation, etc.
		PTC thermistor:	heater element, switch, temperature compensation, etc.
		CTR thermistor:	heat sensor element
		Thick film thermistor:	infrared sensor
		Varistor:	noise elimination, surge current absorber, lighting arrestor, etc.
		Sintered CdS material:	solar cell
		SiC heater:	electric furnace heater, miniature heater, etc.
	Ion conducting materials (β-Al_2O_3, ZrO_2)	Solid electrolyte for sodium battery	
		ZrO_2 ceramics:	oxygen sensor, pH meter fuel cells
Magnetic functions	Soft ferrite	Magnetic recording head, temperature sensor, etc.	
	Hard ferrite	Ferrite magnet, fractional horse power motors, etc.	
Optical functions	Translucent alumina	High pressure sodium vapor lamp	
	Translucent magnesium, mullite, etc.	For a lighting tube, special purpose lamp, infrared transmission window materials	
	Translucent Y_2O_3-ThO_2 ceramics	Laser material	
	PLZT ceramics	Light memory element, video display & storage system, light modulation element, light shutter, light valve	
Chemical functions	Gas sensor (ZnO, Fe_2O_3, SnO_2)	Gas leakage alarm, automatic ventilation fan, hydrocarbon, fluorocarbon detectors, etc.	
	Humidity sensor ($MgCr_2O_4$-TiO_2)	Cooking control element in microwave oven, etc.	
	Catalyst carrier (cordierite)	Catalyst carrier for emission control	
	Organic catalyst	Enzyme carrier, zeolites	
	Electrodes (titanates, sulfides, borides)	Electrowinning aluminum, photochemical processes, chlorine production	
Thermal functions (ZrO_2, TiO_2 ceramics)		Infrared radiator	
Mechanical functions	Cutting tools (Al_2O_3, TiC, TiN, others)	Ceramic tool, sintered SBN	
		Cermet tool, artificial diamond	
		Nitride tool	
	Wear resistant materials (Al_2O_3, ZrO_2)	Mechanical seal, ceramic liner, bearings, thread guide, pressure sensors	
	Heat resistant materials (SiC, Al_2O_3, Si_3N_4, others)	Ceramic engine, turbine blade, heat exchangers, welding burner nozzle, high frequency combustion crucibles	
Biological functions	Alumina ceramics implantation Hydroxyapatite bioglass	Artificial tooth root, bone, and joint	
Nuclear functions	Nuclear fuels (UO_2, UO_2-PuO_2)		
	Cladding material (C, SiC, B_4C)		
	Shielding material (SiC, Al_2O_3, C, B_4C)		

Source: George B. Kenney and H. Kent Bowen, "High tech ceramics in Japan: current and future markets," American Ceramic Society Bulletin, vol. 62, no. 5 (1983), p. 591.

indicates a doubling and redoubling market for ceramic substrates and packages over the next decade. Table 3 provides an estimate of the future market potential for ceramic integrated circuit (IC) packaging in the United States, indicating an impressive annual growth rate of 9 per cent. The difficulties for a new producer are equally impressive. First, a complex existing technology must be mastered and products must be sold in competition with outstandingly expert and efficient producers. Second, the existing technology is likely to be outmoded in a few years by alternate, advanced and proprietary technology.

Table 3. Estimated market potential in the United States for ceramic IC packaging (in millions of $US)

Year	Total IC shipments	Ceramic-based	Percentage	Ceramic package value
1980	6 768	1 692	25	220
1985	13 000	5 200	40	676
1990	27 000	13 500	50	1 755

Source: Based on estimates provided by Candice Stevens, Office of Strategic Resources, U.S. Department of Commerce, Washington, D.C.

Ferroelectric ceramics, primarily barium titanate and related materials, have a high dielectric constant making them excellent as the dielectric in capacitors, which are an indispensable component in electronics. Some are made by a process similar to the multi-layered substrates discussed above. Vast numbers (tens of billions) are required at a low unit-cost and great efforts are being made to lower the cost by using cheaper metals (which must survive firing) as electrodes. Candice Stevens estimates that in 1982 a total of 6,530 million capacitors were shipped in the United States. Of these 5,100, or 78 per cent, were ceramic-based, but these had a value of $452 million representing 38 per cent of the total of $1,190 million for all capacitor shipments. Table 4 provides her estimate of the future market potential in the United States for ceramics in capacitors.

Table 4. The market potential in the United States for ceramics in capacitors (in millions of $US)

Year	Total shipments	Ceramic-based	Percentage	Ceramic value
1980	1 085	390	36	234
1985	1 450	580	40	348
1990	2 000	1 000	50	600

Source: Based on estimates provided by Candice Stevens, Office of Strategic Resources, U.S. Department of Commerce, Washington, D.C.

Piezo-electric ceramics, such as lead zirconate titanate, are used in a wide variety of applications to convert motion into electrical signals and vice versa. Vibrators, oscillators, filters, loudspeakers, among others, are essential parts of many industrial and consumer products.

Ceramic semiconductor materials include titanates, silicon carbide, zinc oxide, vanadium oxide, nickel oxide, iron oxide, and cobalt oxide. In some cases they are used as thermistors, i.e. as strongly temperature-dependent resistors, for temperature control. They are also used as varistors, i.e. as voltage sensitive resistors, to protect against voltage surges during lightning storms and as chemical sensors, by relying on the large changes in electrical conductivity which absorbed chemicals can change on the surface of thin films. In still other cases they are used as miniature heaters.

Ionic conducting ceramics, such as beta-alumina and stabilized zirconia, are finding important uses as oxygen sensors in automobiles and as electrolytes in fuel cells.

Magnetic ceramics, such as ferrites made of iron oxide in combination with one or more of the oxides of barium, lead, strontium manganese, nickel, and zinc, can be tailored to be either hard or soft magnets. They find wide application in loudspeakers, motors, transformers, recording heads and the like. Ceramic ferrites are sometimes considered to be a relatively mature market, but they might be of particular interest to developing countries as their economies develop and they begin to experience the enormous use of small electric motors characteristic of highly developed countries.

Candice Stevens has attempted to estimate the market in the United States for electronic ceramics other than integrated circuit packages and capacitors. Her conclusions are given in table 5.

Table 5. The market potential in the United States for ceramics in other electronic components (in millions of $US)

Year	Total shipments	Ceramic-based	Percentage	Ceramic content
1980	15 600	1 560	10	80
1985	20 000	3 000	15	150
1990	26 000	5 200	20	260

Source: Based on estimates proved by Candice Stevens, Office of Strategic Resources, United States Department of Commerce, Washington, D.C.

In the category of optical functions, a special form of pore-free alumina is widely used as the inner envelope for high pressure sodium vapour lights, whose characteristic orange glow lights so many of the highways of the world. Lead zirconate titanate (PLZT) ceramics are a specialty material increasingly used in light modulation and displays.

Modern high-transmission optical fibres are a material of enormous future technical and economic importance. These are currently silica-based glasses and, as such, are a type of new ceramic. This field is just taking off economically. In 1982 some 373 km of low loss fibre was sold with a value of $335 million. For 1990, sales of 5,271 km with a value of $4,000 million is forecast. The additional field of fibre optic sensors is in an even earlier stage of development. Sales in the United States in 1981 have been estimated at $12 million. The forecast for 1991 is $180 million.

Ceramics play important roles as sensors for fuel/air mixtures, for humidity, and have potential for wider application in the chemical process industry. Semiconducting ceramics (e.g. ZnO) and ionic conductors (e.g. stabilized zirconia) are generally used. Ceramics also serve to promote chemical reactions, as in the case of ceramic catalyst-carriers and ceramic electrodes.

One of the oldest uses of ceramics is as thermal insulators at high temperatures and they continue this role in modern form, e.g. as super insulators such as the silica tile used on the United States space shuttle. Modern ceramics such as silicon carbide and silicon nitride are increasingly attractive as heat exchangers, as are the low-expansion ceramics such as cordierite.

Much of the excitement over new ceramics centres on their improved mechanical properties and their potential use in industrial processes and in heat engines. Major families include silicon carbide, silicon nitride, transformation-toughened zirconia and alumina, and composites involving ceramic fibres.

A potentially important market for new ceramics is as implants to replace teeth, bone, and joints.

Ceramics have long been used in the nuclear field as fuels, cladding material and shielding material. They are leading candidates as matrices to contain radioactive wastes for long-term storage.

Ceramic processing

The outstanding properties possessed by advanced ceramics are achieved through special compositions and microstructures that require very careful control throughout the successive stages of ceramic processing. These stages are summarized in table 6 for the most important type of ceramic processing that involves production of a powder, consolidation into an unfired blank called a "green ceramic", sintering and final finishing.

Table 6. Stages in the processing of crystalline ceramics

Powder synthesis
Powder sizing
Rheology control
Consolidation and forming processes
Sintering
Final machining
Inspection

It is impossible to go into ceramic processing in depth in this paper, but a brief sketch will help in understanding the challenge in making advanced ceramics. Fine grain size is generally desirable in finished ceramics in order to impart high strength and to permit the making of small parts or where smooth finishes are required, for example in substrates for electronic chips. Some chemical synthesis processes directly yield fine powders. Other chemical processes give larger size powders and require an additional step of size reduction through milling or grinding.

Traditional ceramics are largely made from natural raw materials which are physically separated and reduced in size. The new ceramics generally require chemical conversion of raw materials into intermediate compounds, which lend themselves to purification and subsequent chemical conversion into the final form desired. The details of these processes are sometimes trade secrets. An extreme example of production of pure oxide powder would involve refinement of pure metal from an oxide followed by reoxidation under controlled conditions. More typically for oxide powders a soluble intermediate, such as a carbonate, hydroxide, or a metal-organic compound, is formed, purified and then transformed into an oxide. For the carbide and nitride ceramics, high temperature reactions are generally used. At one extreme, a mass of silica sand and coke is heated by current from carbon electrodes (the Acheson process) to produce a large mass of silicon carbide crystals which must then be broken up and sized. At another extreme, very fine and uniform silicon nitride particles can be produced by a laser-driven reaction between silane and ammonia.

Table 7. Powder synthesis

Natural raw materials
Metal purification followed by reaction
Carbonate or hydroxide purification followed by thermal treatment
Precipitation
Gas phase reaction
Use of metal-organic precursors

Traditional ceramics are made using powders which have a distribution of particle sizes. For the new ceramics one experimental line of work aims at producing very strong and reliable ceramics by working from very fine spherical, monodispersed powders (powders having a very narrow distribution of particle sizes). These monodispersed powders are made typically by techniques of colloidal chemistry for oxides and by controlled nucleation and growth in gas phase reactions for the carbides and nitrides. However, most of the new ceramics are still made from powders with a broad distribution of particle sizes but with smaller average particle sizes (less than one micrometer) than the traditional ceramics.

Typical processes for particle size reduction and/or selection are listed in table 8. Air classification and elutriation (settling in a liquid) are processes which separate powders into different size-range fractions. Attrition milling and ball milling are typical of processes that reduce the average particle size but leave a very broad distribution of particle sizes. Thus a two-stage process for reduction followed by separation of particle size fractions may be required. Contamination during these processes is sometimes a problem.

Table 8. Powder sizing processes

Air classification
Attrition milling
Ball milling
Calcining
Elutriation
Fluid energy milling
Freeze drying
Hammer milling
Precipitation
Vibratory milling

Powders are difficult to handle and this difficulty increases as the particle size decreases. The powder must be compacted into a shape approximating the final part before sintering (final compaction by heating to high temperature). This compaction requires a flow which is impeded by agglomeration of the powder particles into clusters. Such clustering can cause pores of sufficient size in the green part such that large flaws can remain in the final ceramic with sometimes disastrous results for strength. Control of the rheology (flow characteristics) of the powder is essential. The powder is effectively made into a more or less viscous fluid by the addition of substances that will subsequently decompose and escape as gases during the early stages of heating before appreciable sintering takes place. Table 9 lists types of additives and the functions which they perform.

Table 9. Types and functions of additives to mixtures for rheology control and other purposes

Additive	Function
Binder	Green strength
Lubricant	Mould release, interparticle sliding
Plasticizer	Rheological aids, improving flexibility of binder films, allowing plastic deformation of granules
Deflocculant	pH control, particle-surface charge control, dispersion, or coagulation
Wetting agent	Reduction of surface tension
Antistatic agent	Charge control
Antifoam agent	Prevent foam
Foam stabilizer	Strengthen desired foam
Chelating or sequestering agent	Deactivate undesirable ions
Fungicide and bactericide	Stabilize against degradation with aging
Sintering aid	Aid in densification

Source: A. G. Pincus and L. E. Shipley, quoted by David W. Richerson, Modern Ceramic Engineering: Properties, Processing and Use in Design (New York, Marcell Dekker, Inc., 1982).

Ceramics are typically very hard and expensive to machine after the sintering stage. It is therefore of overriding economic importance that the green ceramic be shaped into an oversized approximation of the final part desired. If this is done well and shrinkage during sintering is properly taken into account, little or no final machining will be required. Table 10 lists some of the most important consolidation processes for making the shaped green parts.

Table 10. Major techniques for powder consolidation and shape forming

Pressing	Plastic forming
Uniaxial pressing	Extrusion
Isostatic pressing	Injection moulding
Hot pressing	Transfer moulding
Hot isostatic pressing	Compression moulding
Casting	**Other techniques**
Slip casting	Tape forming
Thixotropic casting	Flame spray
Soluble-mould casting	Green machining

Source: Summarized by the authors based on David W. Richerson, Modern Ceramic Engineering: Properties, Processing and Use in Design (New York, Marcell Dekker, Inc., 1982).

In uniaxial pressing, a powder-additive mixture is compacted in a die by applying pressure along a single direction. This typically produces density gradients in the green piece that can persist in the sintered part with undesirable results. The process is also limited in the complexity of green shapes that can be made. More complex parts and more uniform green densities can be made by the more expensive process of isostatic pressing. This process involves the application of pressure uniformly on all sides by enclosing the powder in a liquid-tight rubber mould and immersing the mould in an essentially incompressible liquid that is then pressurized. The powder can first be formed by one of the casting or plastic forming processes and subsequently isostatically pressed so that great flexibility is possible.

Variations of these two processes can be carried out at high temperature, in which case the shaping process and the sintering process are combined. In hot pressing a heated die, typically graphite, is used. In hot isostatic pressing a gas such as argon is used in conjunction with a specimen container, typically metal or glass, that softens at high temperature and transmits pressure uniformly but prevents gas entry into the pores of the partially-compacted ceramic.

Casting is another family of consolidation and shaping techniques. A suspension, called a slip, of the powder in water or organic liquids is prepared with suitable additives for rheology control (frequently one of the critical trade secrets). This slip is cast into a mould having very fine pores. Enough of the liquid is removed into these pores by capillary attraction or external pressure to convert the remaining powder-liquid mixture into a green body having sufficient strength for subsequent handling. The shape is then removed from the mould and further liquid is extracted by drying at a rate which must be carefully controlled to avoid cracking.

Plastic forming constitutes another, somewhat similar family of consolidation and forming techniques. In this case a mixture that is deformable under pressure is made using suitable additives. This is extruded into dies or pressed into moulds, usually with some heating to facilitate plasticity. The binders must be removed by decomposition and evaporation in carefully controlled heating before heating to higher temperatures for sintering.

The sintering action itself is complex. Two processes generally take place simultaneously. The desirable process of densification takes place under the action of surface tension forces. The undesirable process of grain growth takes place under the action of differential grain boundary energies. Some of the additives used in the forming stage of processing are high-temperature materials themselves (such as small amounts of other oxides) introduced to reduce grain growth in normal sintering or to give some high-temperature plasticity in those cases when hot pressing is used. In addition to helping with the processing stage, these additives sometimes affect final properties. Their effect can be beneficial (e.g. electrical conductivity control in grain boundaries) or harmful (e.g. promoting slow creep at high temperatures). The interrelated fields of sintering-additive design and grain-boundary engineering for property control are in themselves complex and critical aspects of ceramic processing.

There are additional processes which combine several steps and avoid or greatly modify the powder processing aspects of conventional ceramic processing. Glass-ceramics are made by melting the components together as a glass-forming liquid, forming the articles by glass-forming techniques and then crystallizing the glass with a subsequent heat treatment using the aid of a nucleating agent that causes many small crystals to grow, simultaneously resulting in a largely crystalline, fine-grain ceramic of high strength. The process is limited to glass-forming systems. Sol-gel processing begins with metal ions in metal-organic compounds that can be put in solution and mixed on the molecular level, thus achieving homogeneity in multi-component systems on a fine scale that is difficult or impossible to achieve by powder mixing. These metal-organics are reacted, typically with water, to simultaneously form oxides and to form polymers which develop strength and so become a gel. These are dried (with large attendant shrinkage, a problem with the method) and then heated to sinter into the final product.

A central problem in ceramic processing is to avoid the formation of flaws during any of the early stages. For high-strength applications, flaws with a maximum dimension of 100 micrometers may be unacceptable. This is the origin of the famous reliability problem of ceramics that necessitates proof testing every part for the most demanding applications. Improvements in reliability through improvements in processing control is perhaps the greatest challenge for advanced structural ceramics.

Some major families of advanced ceramics

There are some families of advanced ceramics that are attracting a great deal of attention because of the new markets which they promise to serve and because of the excitement associated with their rapid technical progress.

Silicon nitride has been attracting great attention and is one of the frontrunners for great growth. It occurs in both alpha and beta phases so that phase purity as well as purity in the ordinary sense become important. Powders with an alpha phase content of approximately 90 per cent and with a mean particle size around 0.7-1.0 micrometer are available from several manufacturers. These powders are difficult to sinter, in part because of the high dissociation pressure at high temperature, so that pressurized sintering methods are used to produce either hot pressed silicon nitride (HPSN) or gas pressure sintered silicon nitride (GPSSN). Small amounts of oxides are usually added to facilitate sintering and allow the production of ceramics with high strength and very attractive short-term properties.

Table 11 compares basic physical properties of competing structural ceramics and table 12 compares properties of these materials which are strongly dependent on the microstructure formed during sintering and so can vary considerably for the same nominal material. Unforturately, the oxide sintering aids cause long-term loss of strength at high temperature (above 1,000°C). A different approach is to form a green ceramic from silicon powder by cold pressing a porous part and then converting the part to silicon nitride by reacting with nitrogen at high temperature. This results in a body which has a lower initial strength but which retains this strength for a long time at high temperature. Evidently the choice of the type of silicon nitride to use must be tailored to the conditions of application. Intense research is directed towards effective sintering aids that allow good strength retention at high temperature. Production of better powders is also being attempted, but the market, although potentially large, is still primarily a market for research material. Therefore, investment in production capacity for powders is risky.

Tables 11 and 12 provide a perspective of the relative advantages and disadvantages of the competing advanced ceramics, thus illustrating that silicon nitride has low thermal expansion, good for resisting thermal shock but bad for use in conjunction with iron-based alloys.

Silicon carbide is a major competitor with silicon nitride for the first generation of advanced structural ceramics. Long used as an abrasive and available as a silicon-bonded material, it entered a new era with the discovery of methods to sinter to full density with suitable sintering additives. It occurs in both alpha and beta phases and both have now been sintered to full density. Both silicon carbide and silicon nitride possess excellent strength and moderate toughness. The properties of either material appear adequate for many industrial and heat engine applications. Work centres on reliably achieving these properties in complex shapes - one of the great technological contests of the world.

Partially stabilized zirconia (PSZ) has been in limited use for decades. Without stabilization, zirconia rapidly transforms from a monoclinic form to a tetragonal form and back again upon heating and cooling. The addition of a sufficient amount of a stabilizing oxide (e.g. 10 per cent magnesium oxide) keeps zirconia in the cubic phase. Partial stabilization yields a cubic phase including a transforming phase. A discovery was made some ten years ago that, if the particles of the transforming phase were kept well below 1 micrometer in size, the strength and toughness were dramatically improved. This opened a new period in structural ceramics. As table 12 shows, strength values above 700 MPa and toughness above 8 MPa mexp(1/2) are commercially available, and still better PSZ materials are in the research stage. The good thermal expansion match for iron-based alloys, the reasonable hardness, and the low thermal conductivity makes PSZ an outstanding candidate for use as a structural material. Its use will probably be limited to moderate temperatures, however, because the strength typically drops to half at 700°C and to one-fourth at 1,000°C.

Table 11. Comparison of some basic properties of selected compounds used in advanced ceramics

Compound	Density (g/cm^3)	Hardness (kg/mm^2)	Melting point (°C)	Thermal conductivity (cal/(cm.s.°C))
Aluminium Oxide	3.98	2 100	2 050	.07
Zirconium Oxide 1/	6.27	1 200	2 715	.005
Silicon Carbide	3.22	2 500	2 220 2/	.16
Silicon Nitride	3.17	2 400	1 900	.04
Silica Glass	2.20	--	--	.002

1/ Stabilized in cubic form.

2/ Decomposes.

Table 12. Comparison of properties important to structural use for some advanced ceramics

Material	Strength (MPa)	Toughness (MPa mexp(1/2))	Thermal expansion (10 exp(-6)/°C)
		<u>Types of Silicon Nitride</u>	
RBSN	300	3.6	3.3
HPSN	1 100	6.6	3.5
GPSSN	440	2.9	3.5
		<u>Types of Silicon Carbide</u>	
Alpha SSC	420	2 to 3	4.1
Beta SSC	533	2.4	4.1
HPSC	800	3.9	4.2
		<u>Types of Transformation-toughened Ceramics</u>	
PSZ	700+	8+	10.2
TTA	900	8.0	7.0
		<u>Ceramic-Ceramic Composites</u>	
SiC-LAS	620	15.0	1 to 4

<u>Key</u>

RBSN	Reaction bonded silicon nitride
HPSN	Hot pressed silicon nitride
GPSSN	Gas pressure sintered silicon nitride
Alpha SSC	Alpha-phase sintered silicon carbide
Beta SSC	Beta-phase sintered silicon carbide
HPSC	Hot pressed silicon carbide
PSZ	Partially stabilized zirconia
TTA	Transformation-toughened alumina
SiC-LAS	Silicon carbide fibres in lithium aluminosilicate glass

<u>Aluminium oxide</u> is available as a powder with 99.99 per cent purity and average particle size of about 0.5 micrometer. The existing markets for sodium vapour lamp tubes and electronic ceramics make this a well-supplied, competitive business. Strengths above 350 MPa can be obtained by conventional sintering and values around 700 MPa by hot pressing, but the latter are expensive and limited in shape. However, the low toughness value of this material limits its consideration as a structural material. The extension of the transformation-toughening mechanism used in partially stabilized zirconia to make transformation-toughened alumina (TTA) is dramatically changing this picture. As table 12 shows, strength and toughness values comparable to PSZ are being achieved in TTA in research specimens. Only some 15 per cent of the more expensive zirconia is needed in TTA, together with the cheaper alumina, so that the prospects for TTA seem very good.

The final example of an advanced structural ceramic to be considered are the so-called ceramic-ceramic composites. These consist of ceramic fibres (typically silicon carbide) in a glass or glass-ceramic matrix. Excellent strengths up to 1,000°C and high toughness values (in the range of metals) have been achieved, as illustrated in table 12. These materials are currently made by hot pressing, which is expensive and shape-limiting. Also, oxidation problems associated with cracking of the matrix have emerged. They will undoubtedly find important specialty uses and as such form the third generation of advanced structural ceramics.

Potential impact of new ceramics on developing nations

So far, this article has concentrated on families of advanced ceramics which are new and are still undergoing rapid change. However, a predominant part of the present market for ceramics is made up of better established and more traditional ceramics. Some of these established ceramics are sophisticated, high-technology materials, such as spark-plug porcelains. Other portions of established ceramics are likely to develop more high-technology products as materials and processes improve. For this reason and because the established ceramics appear to offer the best prospects for developing nations, the interplay between the high-ceramic technologies being developed for the new ceramics and future possible improvements in established ceramics will now be discussed.

Some established ceramic industries are compared with new and rapidly changing industries in table 13. The refractories industry has been concerned with ceramics for insulation, chemical erosion, and resistance in high-temperature furnaces for steel making, glass melting, and similar uses. The new ceramics intended for service in heat engines are, in one sense, special types of refractories with the added need to carry substantial loads in some engine application. They are being developed primarily by scientists and engineers outside the traditional refractories community, but the new technologies which they require will also undoubtedly lead to improvements in traditional refractories.

Table 13. Typical established ceramic industries compared with new ceramic industries

Established and evolving	New and rapidly changing
Refractories	Structural heat-engine ceramics
Whitewares	Wear-resistant specialty ceramics
Electrical ceramics	Electronic ceramics
Flat and container glass	Optical communication glass
Cement and concrete	Composite involving cement
Mineral resources	Synthetic powders and fibres
Enamelled metals	Ceramic fibre reinforced metals
Co-WC cutting tools	Ceramic cutting tools
Ceramic nuclear fuels	Nuclear waste disposal ceramics

Table 14 illustrates schematically that an established industry is subject to two kinds of forces to modify products, in addition to the normal pressures of economic competition in their established product line. One force results from changes in the requirements of the market that they serve, such as the increasing use of continuous casting by the steel industry and the associated need for special refractories for this casting technology. The other force results from developments in ceramic technology that can be used to produce improvements in traditional products or in products for new markets. As ceramic technology advances, giving products with higher performance and longer life, the value of these products per unit weight increases. This makes shipping over long distances economically possible and increasingly makes ceramic industries subject to world-wide competition. A manufacturer of an established type of ceramic product cannot afford to ignore developments in high technology ceramics that could be applied to improve his type of product. It may seem that since such a gap exists between the complex and expensive technologies used with the new ceramics and the relatively low cost of many traditional ceramics, the former would have no impact on the latter. It is believed that there will be many significant impacts from fundamental aspects of the new technologies, although these will require adaptation to traditional products.

Table 14. Forces of change acting on established ceramic industries

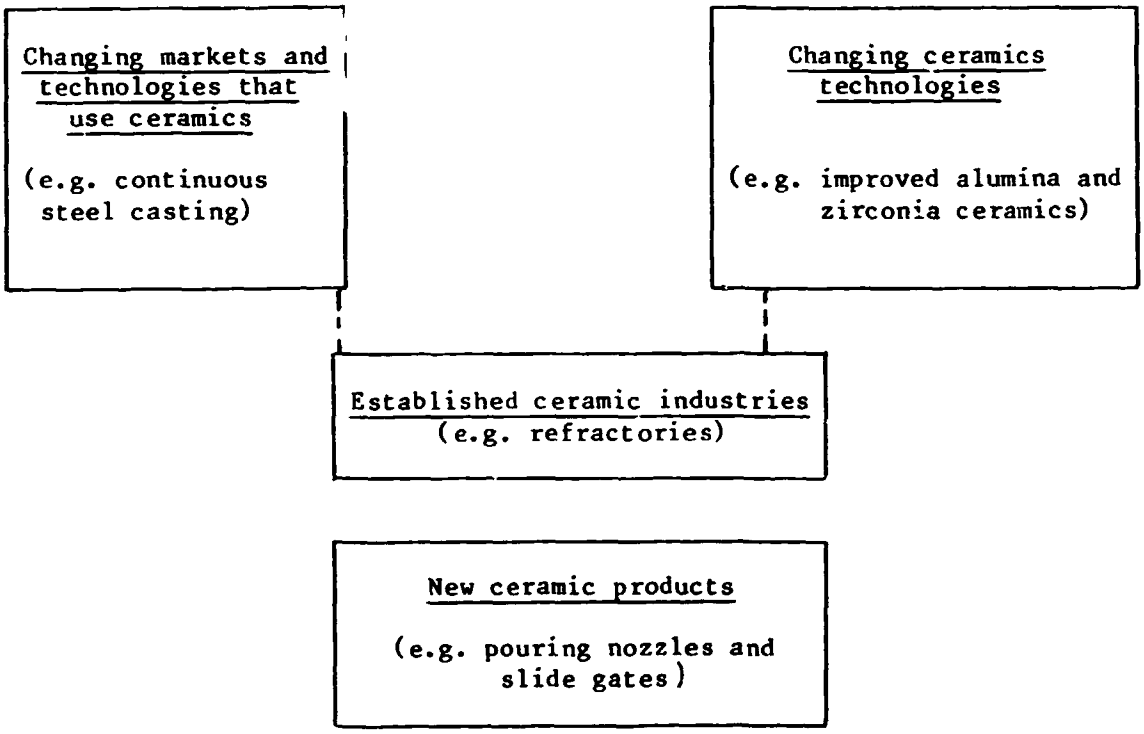

Table 15 provides more detail on recent changes in the steel-making refractories industry. The special refractories required for the list of new steel-making processes are sophisticated, high-technology products in their own right, even though they are typically not as costly or difficult to make as some of the newest ceramics.

Table 15. Examples of new ceramics requirements for the steel industry

Steel industry process changes	Ceramic material changes
Direct reduction	Tar-bonded dolomite Carbon magnesite refractories used in reduction vessel
Electric melting furnace	Newest chrome-magnesite brick grain for brick New graphite and composite electrodes
Continuous steel casting	Alumina-carbon tubular shrouds for pouring steel from ladle to tundish and from tundish to column Zirconia and alumina slide gates for control of steel flow from tundish
Billet transfer	Fused cast chrome magnesite slabs for wear resistance

Table 16 lists some of the fundamental ceramic technologies being developed for use in making new ceramics. Some of these technologies very likely can be adapted to give better products in many of the established ceramic industries listed in table 13. For example, the work on fine powders, chemical routes to green bodies and better rheology control may well lead to the development of bulk ceramics made with a bonding phase of very fine particles in a material predominantly made up of larger grains of a relatively iexpensive ceramic.

Table 16. Fundamental ceramic technologies in the process of development for new ceramics

Ultra-fine, ultra-pure ceramic powder production
Improved powder size distributions
Chemical routes to green ceramics (e.g. sol-gel)
Chemical routes to final ceramics (e.g. chemical vapour deposition (CVD))
Improved dispersion and rheology of slips and injection moulding mixtures
Pressure-assisted slip casting
Injection moulding
Hot pressing and hot isostatic pressing
Improved sintering aids
Grain-boundary engineering
Toughness control through second phases
Ceramic composites technology
Finer-grain thin-layer ceramics for electronics
Thermal expansion matching ceramics for silicon
Ultra-low optical absorption glasses
Protective ceramic thin-films and coatings
Composites and gradient-composition ceramics for ceramic-ceramic and ceramic-metal joining

Developing nations should study the progress in new ceramics from two points of view: first, to find a portion of the process of making one or more of the new ceramics that they could profitably perform and, second, to find portions of the new technologies associated with the new ceramics that they can adapt to the production of the more well established types of ceramics. Table 17 provides overall analysis of the likelihood of success classified according to whether a market is domestic or external, and whether the nation involved is developed or developing. A developed nation with strong technical capability presumably can take full advantage of the economic potential of existing ceramic technologies as they apply to that nation's particular raw materials and market conditions when the market is domestic. Excellent possibilities also exist for the new ceramics for domestic markets. A developing nation has a strong likelihood of being able to transfer new ceramic technologies in existing industries as they are adapted to these industries, at least for domestic markets. Their chance of being able to develop profitable industries for the new ceramics for their domestic markets appears quite small, in part because a whole user-industry for the new ceramics would have to be developed as well.

Table 17. Estimates of the potential for technology transfer in developing and developed nations to serve domestic and external markets (Percentage)

Countries	Existing ceramic industries	New ceramic industries
	Potential use for domestic markets	
Developed	100	80 to 100
Developing	80	0 to 5
	Potential use for external markets	
Developed	80 to 100	40 to 80
Developing	25 to 50	40

With respect to the potential for new ceramic technologies to make products for export markets, a somewhat different situation appears probable. Developed countries again have excellent prospects for applying new technologies to established products appropriate to their raw materials and economic circumstances. For new ceramics the prospects are good but hazardous due to the difficulties involved with the new ceramics and the fierce international competition that is likely to develop. On average, developing nations would seem to have only fair prospects for adapting new technologies to traditional ceramics for export because they will probably enter this market later than the developed countries. There may be exceptions to this generality when a cost advantage for the developing country can be combined with a joint venture with a multinational firm that has already mastered the technology and has marketing arrangements outside the developing country. For the new ceramics themselves, some developing countries may be able to offer labour-cost advantages, but the complexity of the new ceramics technologies probably makes a joint venture with an outside leader in the field almost essential. It is appropriate, therefore, to consider the lessons of experience in the transfer of ceramic technologies to developing nations.

How ceramic technology is transferred to developing nations

For the transfer of technology in ceramic materials to occur in any nation, there must be a basis for utilizing the materials within that country or in an export market. Therefore, this is likely to be an evolutionary process rather than a revolutionary process. In a developing nation, the transfer of the highest technology of ceramic materials can only occur if the transferring agent or country were to act as the recipient of the produced materials from the developing country or as the distributor of these materials for that region. The incentive for the transfer of technology would be the favourable labour rates and essentially more economical production of those materials.

As stated previously, the term "high technology" should include the advances in the technological state of the more mature ceramic industries. These industries could supply technology for the pattern of developing needs in each of those nations. Examples might be refractories, whitewares, cements, ceramic metal systems, structural clay materials, glass and electrical ceramics. Many examples could be given of developing countries that have had technology transfer in ceramics to implement their existing and growing industry. Two country case studies will serve to illustrate how technology may be transferred to a developing nation.

The first study deals with the transfer of refractory technology to a country in Eastern South Asia. There were many raw materials available for refractory use in this country, but the existing industry was extremely poor and not well managed on a scientific and engineering basis. A manufacturer from the United States surveyed the needs throughout the world for possible technology transfer and licensing arrangements and selected this country. Contact was made in 1970 and, after a round of negotiations, an agreement was signed in 1973. This company had 30 different products as candidates for technology transfer. In order to accomplish this technology transfer, it was necessary to instruct the engineers of that country in the various methods of material characterization and the technology of modern production techniques. By 1974 one product of low technical importance had been transferred and was available on the market. At this point geologists were employed to search the country for additional raw materials and to develop an even better characterization laboratory and beneficiation techniques. During the next ten years, most of the 30 different products were transferred to the developing nation, but all along the way support was required from the licensing company with respect fo carrying out laboratory analyses, making technological assessments, and slowly equipping a modern laboratory. Initially, the materials were transferred from Eastern South Asia to the United States for evaluation and development in actual pilot plant operations to prove the feasibility of the product. After the feasibility of the materials was determined, the technology was again transferred to Eastern South Asia.

Perhaps the most important thing to understand is that this evolutionary development required only 14 years. This is a relatively short period for the transfer of technology and speaks well of the technical abilities and assistance programmes generated by the licensing corporation.

The second study deals with a country in South America and had an even longer time frame for developing the technology transfer. In 1965, an emerging ceramic industry in this country was totally dependent upon imported raw materials. In fact, 95 per cent of all materials used in their whiteware plants were from overseas. Of course, this was an intolerable position, both from economic and technological standpoints. As in the first study, the geologists from the corporations began a search for available and usable raw materials for their industry. Using outside consultants and licensing arrangements from the United States, technical criteria and characterization techniques were determined and used as specifications for the whiteware industry in that country. Over time the characterization techniques of the materials became part of the everyday existence of the company and resulted in greater utilization of the indigenous materials of the country. In fact, today 95 per cent of all material used in the whiteware industry is indigenous material. When this technology was transferred, it was certainly considered by that developing country as high technology. Once the basis of a good ceramic industry was developed, the next levels of high technology ceramics were installed. These were in the areas of spark-plugs, ferrites, special glasses, etc. An evolutionary base had matured to the point where the higher technologies could be transferred. It should be pointed out again that this effort started in 1965 and that only now can one see the emergence of some truly high-technology products in that developing country.

There is a scenario that should be examined, and that might best be termed an offshore operation. In this case, a major high-technology corporation might be seeking a highly intelligent work-force located in a country where labour costs are lower than those of developed nations. In this instance, the transfer of technology could be accomplished either by a partnership or by utilizing the low labour costs. The developing nation could share in the marketing of the product by acting as a regional distribution centre for high-technology products and also sending the product to its partners.

The transfer of high-technology ceramics to a developing nation that can assimilate the products into its own infrastructure on an evolutionary basis is probably the preferable model to be followed. There are many partners that could be assembled in order to give the greatest spectrum of skills to implement the transfer. These partners could include major corporations whose technologies can be sold or licensed on appropriate terms. One effective group is the retired executives organization International Executive Service Corps (I.E.S.C.), with headquarters in Washington, D.C. This organization recommends highly skilled and qualified people to work in developing nations that require assistance in particular ceramic fields. Many leaders of the United States ceramic industry have participated in such programmes throughout the world. The results of this type of input have been enormously successful and, again, this has been an evolutionary process.

An alternative model: technology build-up within a developing country

An alternative model to assist developing nations to enter directly into the high-technology ceramics field could be considered. The major impetus for this entry would have to stem from one of two sources: either the Government of that nation, in order to build both internal and external markets, or a private corporation within the country that can afford the full range of necessary ingredients. The ingredients of a successful programme are enumerated in table 18.

Table 18. The ingredients of a successful programme

1. Capital for facilities.
2. Marketing and sales skills - foreign and domestic.
3. Trained technical personnel.
4. Trained technicians.
5. A competent work-force.
6. Competitive labour and production costs.
7. Educational facilities.
8. Proper characterization tools.
9. Modern production equipment.
10. Confidence in the market in competition with other areas of capital requirements of the country-perceived profitability.
11. Effective management.

When trained personnel are not available in the developing nation, personnel could undergo high-level technical training in a developed country, sponsored either by the Government or industry. In order to enter this high-technology ceramic market, it is essential to train enough students to develop a critical mass of trained scientists and engineers. Trained personnel for auxiliary functions, such as the use of characterization tools and equipment to support the ceramic engineering staff effort, are also required. In addition, technicians must be trained to support the special ceramic-formulation techniques and testing necessary to support the technical staff. This requires a long-term commitment, and it will be necessary to spend considerable money on this education process.

It is not entirely reasonable to try to impose high-technology ceramics on an existing, mature ceramic industry and expect that it can then compete effectively on an international basis in the market place. High-technology ceramics require a degree of quality control that is generally much greater than in conventional ceramics. This requires not only new equipment, but a different attitude and more knowledge. However, a background in traditional ceramics is helpful. There are possible models involving industry, Government, foreign corporations, and international organizations. In table 19 possible combinations are presented with speculations as to the time of fruition of these ventures and the probability of success. Perhaps other models are possible, but they are not apparent.

Conclusions

New ceramics constitute a commercially important set of materials with good prospects for rapid market growth. The full extent of future growth depends upon further technical developments. Intense competition exists among different families of new ceramics, between ceramics and other materials, and among firms in many developed countries for shares in the new markets.

The new technologies being developed for synthesis and production of the new ceramics will have important impacts upon upgrading the types of ceramics already made by established industries. International competition among suppliers of these ceramics will probably increase.

The low labour costs of developing countries create the potential for sharing in markets for both new ceramics and improved forms of established ceramics. However the technical difficulties and the need for marketing arrangements strongly favour joint ventures with firms from developed nations that have mastered the technology and already are suppliers. The required training of the labour force and acceptance of the typically long time frame are important to understand.

Bibliography

Anonymous. Giants in Ceramics USA. Ceramic industry, v. 121, 1983:20.

Anonymous. Giants in ceramics international. Ceramic industry, v. 121, 1983:37.

Anonymous. New ceramics market in Japan. Tokyo, Yano Research Institute, Ltd. 128 p.

Anonymous. Raw materials handbook. Ceramic industry, v. 120, 1983:31.

Anonymous. New ceramics. Tokyo, Showa Denko.

Table 19. Who Can Initiate High-Technology Ceramic Programmes in Developing Nations: Alternative Models

Initiator	Can provide an education system	Can provide money	Can provide technology	Can provide (or attract) a suitable work-force	Can provide marketing and sales	Needs partner(s)	Probability of use of partners	Probability of success in 5 years*	Probability of success in 10-20 years*	Probability of failure*
National Government	Yes	Yes	Pay for development or purchase	Yes	Yes Train or purchase	Yes Foreign technology, industry, universities	Medium	Low	Medium	Medium
Local government	Yes	Yes	"	"	"	"	Low	Low	Medium	Medium
National industry	No	Yes	Acquire or develop	"	"	Yes Universities, national Government	Medium	Low	Medium	Medium
Foreign industry	Yes	Yes	Yes	No Must use national labour	Yes	Yes national Government, industry	Medium	Medium	High	Low
International organizations	Yes	Yes	No	No	No	Yes national Government, national industry	Low	Medium	Medium	Medium
Individuals	No	Yes	Yes	No	Yes	Yes national Government, State government, Technology Centre	Low	Medium	Medium	Medium

* Estimated by authors as either high, medium or low probabilities.

Anonymous. Development of structural fine ceramics in Japan. Japan industrial and technological bulletin, special issue no. 15, 1983. 28 p.

Anonymous. 1983 Ceramic company directory. American Ceramic Society bulletin, v. 63, 1984.

Hecht, J. Fiber optics turns to sensing. High technolcgy, July/August 1983:49.

Hench, L. L. and Dove, D. B. Physics of electronic ceramics. Marcel Dekker, 1972. 1,116 p.

Kenney, George B. and Bowen, H. Kent. High tech ceramics in Japan: current and future markets. American Ceramic Society bulletin, v. 62, no. 5, 1983:590.

Keck, D. B. and Love, R. E. Fiber optics for communications. Applied optics and optical engineering, v. VI, 1980:439.

Kingery, W. D., editor. Ceramic fabrication processes. Cambridge, Massachusetts, MIT Press, 1963.

McLean, A. F., Ceramic technology for automotive turbines. American Ceramic Society bulletin, v. 61, 1982:861.

Nakajima, Kunio. The fine ceramics industry in Japan, Journal of Japanese trade and industry, no. 5, 1983:15.

Onoda, G. Y., editor. Ceramic processing before firing. New York, John Wiley and Sons, Inc., 1978.

Palmour, Hayne, III, Davis, R. F., and Hare, T. M., editors. Processing of crystalline ceramics. New York, Plenum Press, 1978.

Pincus, A. G. and Shipley, L. E. The role of organic binders in ceramic processing. Ceramic industry, v. 92, 1969:106.

Richerson, David W. Modern ceramic engineering: properties, processing, and use in design, Marcel Dekker, Inc., 1982. 399 p.

Stevens, Candice. Advanced ceramic materials: an assessment of U.S. markets. Washington, D.C., U.S. Department of Commerce, Office of Strategic Resources, in press.

Tallan, N. M. Electrical conductivity in ceramics and glass. Marcel Dekker, 1974. 673 p.

Van Vlack, L. H. Physical ceramics for engineers. Addison Wesley, 1964. 342 p.

Wachtman, John B. Jr. Ceramic fever: advanced ceramics in Japan. Ceramic Industry, v. 121, 1983:24.

Wang, F. F. Y., editor. Ceramic fabrication processes. New York, Academic Press, Inc., 1976.

* * * *

ADVANCES IN THE PROCESSING OF HIGH-TEMPERATURE CERAMICS

Mir Akbar Ali *

In the fabrication of high-temperature fine ceramics, one of the important parameters is the particle size of the material. Finer particles have larger surface area, resulting in improvements in inter-granular reactivity. Traditionally, the production of ceramic powders has involved reducing the size of coarser materials by some form of grinding. Rustum Roy 1/ developed the sol-gel method, followed by a simple and novel technique which is known as Evaporative Decomposition of Solution (EDS) and, as the name implies, falls in the category of solution techniques. 2/ The process is unique due to the fact that the desired fine powders are produced directly from a salt solution in a continuous process. The solution is atomized into very fine mist, the solvent driven off and the remaining salt decomposed, all in a matter of seconds. Due to the small size of the solution mist droplets and the very short time required for completion of the treatment, the atomic scale mixing achieved in the starting solution is preserved in the final powder. In addition, the EDS process can be scaled up for industrial application.

The equipment consists of an atomizer for converting the starting solution mix into fine mist droplets, a furnace for decomposing the droplets and an electrostatic precipitator for collecting the fine powder. Figure 1 is a schematic diagram of the atomizer, which is the main part of the process and equipment. Powders prepared by the EDS process are highly reactive and vastly superior to conventionally prepared powders. This was successfully demonstrated with ferrite compositions.

The U.S. Federal Bureau of Mines recently developed a patented technique for producing sub-sieve size ceramic materials, known as the attrition grinding process. 3,4/ The technique involves intense agitation of a slurry composed of the materials to be ground, a granular grinding medium and a suspending fluid. Preliminary studies were conducted on a 5-inch diameter attrition grinder. With progressive success, the diameter was increased to 10 inches and 20 inches. Figure 2 presents the machine drawings for a 20-inch attrition grinder. Figures 3, 4 and 5 are the schematics and flow sheet of the process. Using this process, a variety of ceramic minerals (mica, pyrophillite, tole, marble, fluorite and anthracite), metal powders (aluminium and copper) and silicon carbide were successfully ground to fine powders.

More recently, fabrication of high-temperature ceramics by the pyrolysis of organometallic polymers has attracted considerable attention. The pyrolysis of silicon containing polymers was developed to produce silicon carbide (SiC), silicon nitride (Si_3N_4), boron nitride (BN) and boron carbide. 4-7/ The technique provides an important opportunity for producing very pure sub-micron powders for the manufacture of non-oxide high-temperature ceramics. The possibility of coating ceramic bodies by dipping, spraying or slurry processes and its use as a binder application has also been demonstrated. 8-10/

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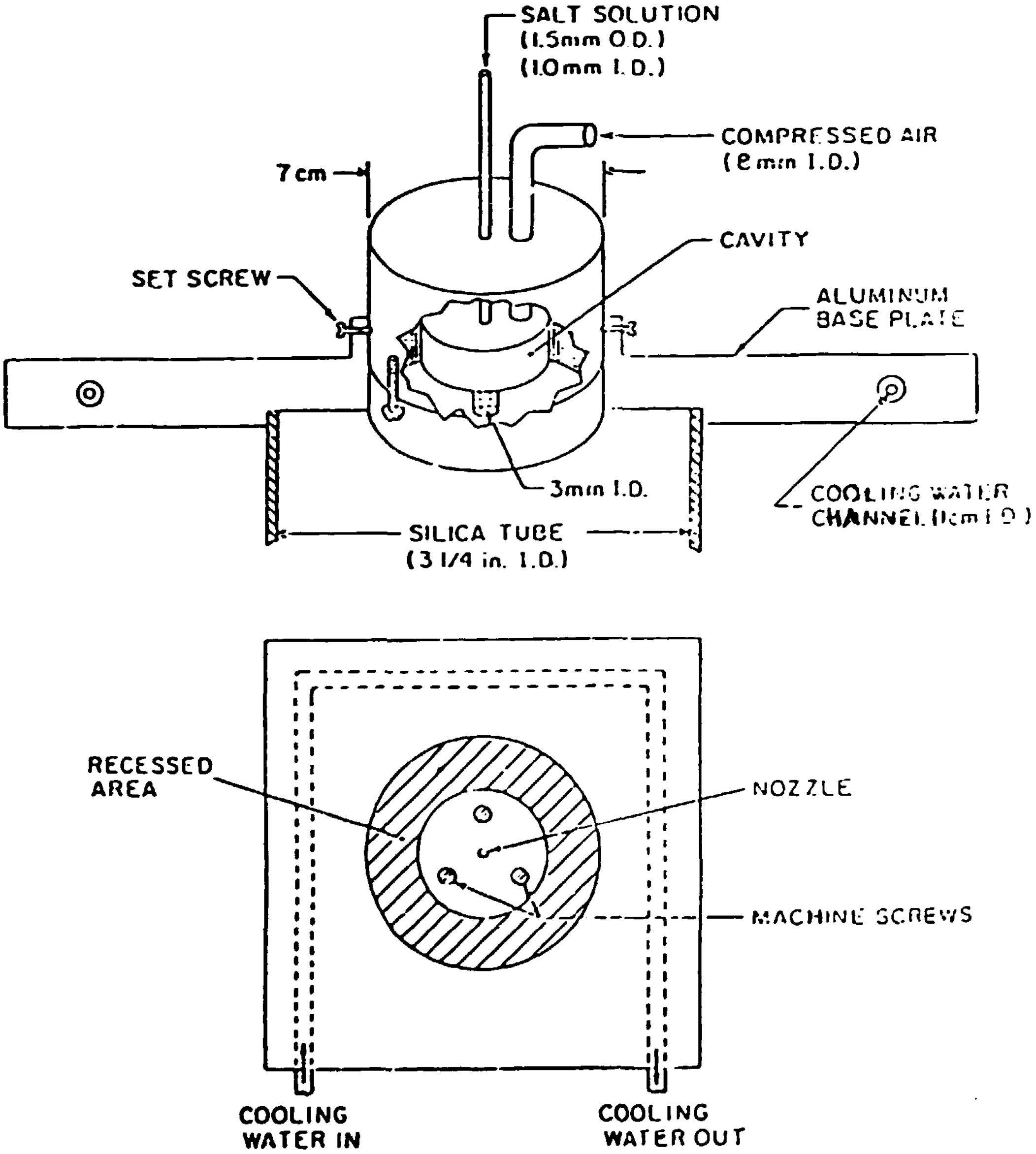
* Glass and Ceramics International, Inc., Lomita, California, United States of America.

Figure 1*. Schematic drawing of the EDS atomizer unit 2/



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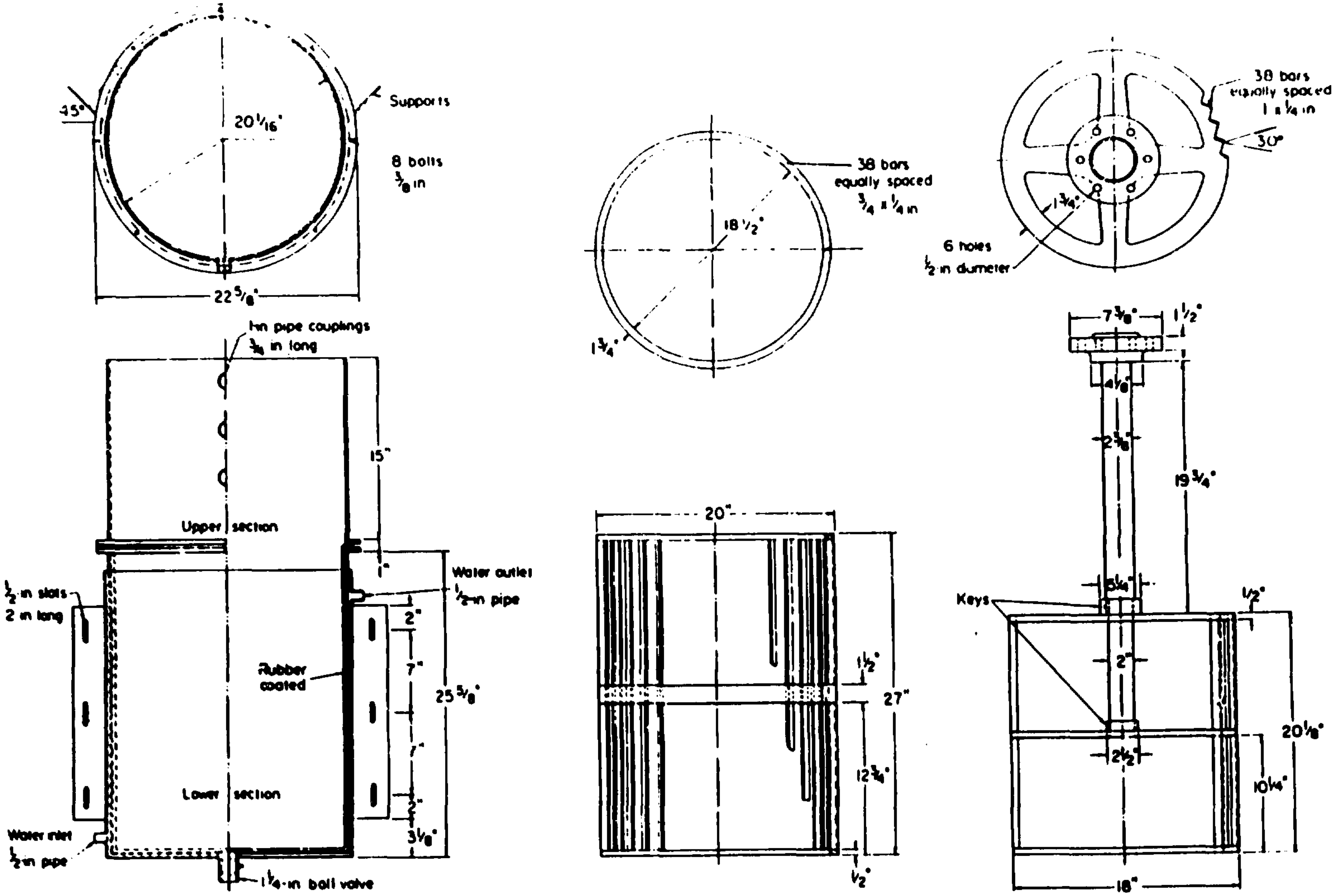

A. CONTAINER ASSEMBLY *B.* STATOR ASSEMBLY *C.* ROTOR ASSEMBLY

Figure 2*—Grinding components in the 20-in-diam attrition grinder. 3/

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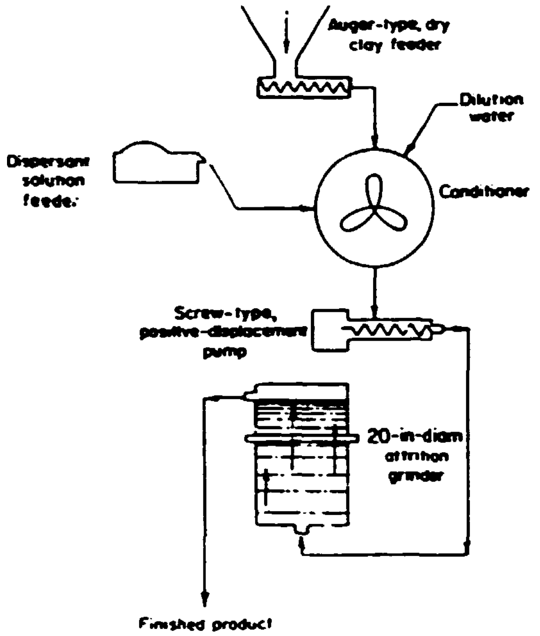

Figure 3*—Schematic flowsheet of continuous open-circuit grinding. 3/

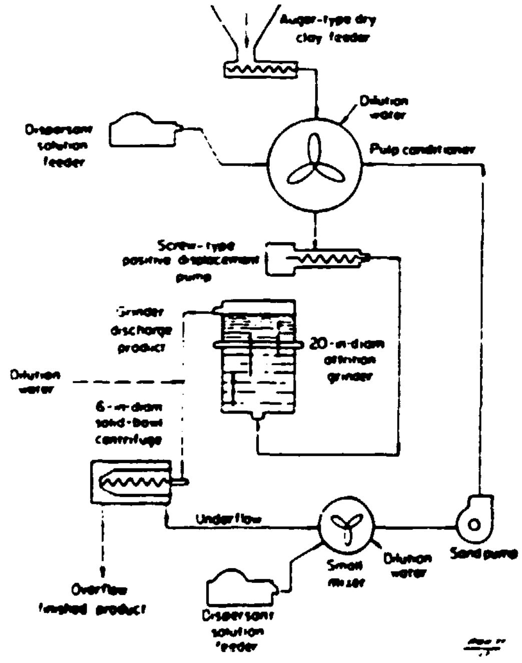

Figure 4*—Schematic flowsheet of continuous closed-circuit grinding. 3/

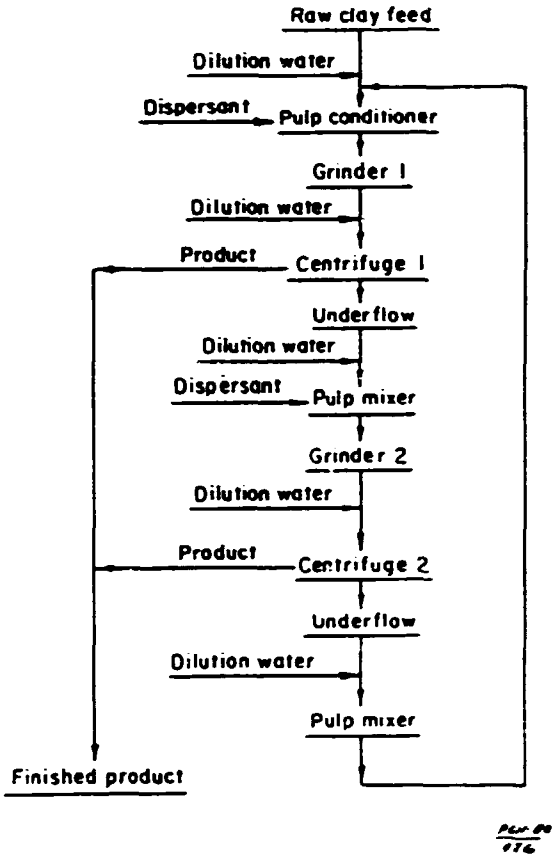

Figure 5*—Flowsheet of modified two-stage, closed-circuit grinding system. 3/

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Fabrication processes

There are three processes for making conventional ceramics. As a result of modifications and improvements, they have been successfully utilized for fabricating advanced ceramics. These processes are: slip casting, ceramic injection moulding and hot isostatic pressing (HIP).

Slip casting is an age-old technique for inexpensive fabrication of ceramic pottery for common use. 11/ However, in the last decade or so, this simple process has been effectively utilized for the development of high-temperature ceramics. In conventional slip casting, the slip consists of solids (clay) and water as the suspension liquid, wherein the solid particles do not chemically react with the liquid. In the fabrication of high-temperature ceramics, such as magnesium oxide (MgO), the potential for reaction was eliminated by making the slip in absolute ethanol. 12/ The word "reaction" refers to preferential absorption of trace amounts of water present in organic liquids (such as alcohol) and the formation of "liquid bridges". The rest of the process is similar to conventional slip casting.

Tungsten is one of the more difficult metals to fabricate, particularly in complex shapes. However, tungsten powders, methyl chloroform and similar organic liquids were successfully combined to form a non-reactive slip for use in the slip-casting process. 13/ More recently, reaction bonded silicon nitride (Si_3N_4) was successfully prepared. 14/ Although the formation of Si_3N_4 from silicon (Si) raw material involves a volume expansion of about 20 per cent, this was overcome by using a synergistic approach wherein the raw batch included a selected percentage of powdered Si_3N_4 as a dimensionally stable filler (grog). Similarly, tin oxide, a high-temperature refractory material, has been successfully slip cast into crucible shapes for melting optical glasses. 15/ Conventionally, optical quality glasses are melted in platinum crucibles and the development of low cost tin oxide crucibles is, in effect, a substitution for expensive platinum.

Ceramic injection moulding is a fabrication process which is extensively used in the plastic industry. The process is fast, versatile, and can easily fabricate intricate shapes. However, during the past decade, interest in the use of ceramics as high-temperature structural materials has grown significantly. In the 1970s, the use of ceramics in the hot flow path of vehicular gas-turbine engines and some diesel engines was extensively investigated. From the existing high-temperature ceramic materials, dense silicon nitride and dense silicon carbide are the most likely candidates. The ceramic components must meet strict dimensional tolerances and maintain very high reliability in use. Even so, it is a prerequisite to produce these components in large quantities at competitive prices. Several fabrication techniques were evaluated. However, component complexity and the need for large production quantities indicated that a technologically and economically feasible fabrication technique would be injection moulding.

The ceramic injection moulding process is not new. A review of literature indicates that during the late 1930s, German industry had used the process for fabricating a variety of ceramic intricate shapes, including spark-plugs. During the same time frame, the ceramic injection moulding process was also patented for a variety of applications. 16-22/ Currently, the need for fabricating high-temperature ceramic materials for gas turbines, turbine rotor blades, combustion chambers and similar components has focused the attention once again on this process. 23,24/

Both Reaction Bonded Silicon Nitride (Si_3N_4-RBSN) and Reaction Sintered Silicon Carbide (SiC-RS) have been shown to be important high-temperature ceramic materials for gas turbines and similar applications, and the injection-moulding process can be used for fabricating complex shapes. Silicon powder and the nitriding aid, which is Fe_2O_3, are mixed with a wax binder and injection moulded. 25/ Following binder removal, the green compact is reacted with nitrogen to form a reaction bonded Si_3N_4 component. Using this technique, another high-temperature ceramic material, aluminium oxide (Al_2O_3), has been successfully injection moulded. 25/ A variety of Al_2O_3 components of complex shapes have been fabricated.

Hot isostatic pressing (HIP) by itself has been an important ceramic-forming process for many years, wherein fine powders in the presence of a binder are pressed to form different shapes. There are two basic processes: cold isostatic pressing and hot isostatic pressing. In both cases, high pressure is uniformly applied to the mould (casing), therefore the name isostatic as opposed to uniaxial in a conventional die compaction. In hot isostatic pressing, heat is provided by resistance heaters in a pressure vessel wherein an inert gas, usually argon, is used as a pressure medium. Typical pressures are around 30,000 psi and the temperature ranges to 2,000°C. The compaction time is between 1 hour and 8 hours. For successful hot isostatic pressing, all three variables, pressure, temperature and time, must be precisely controlled. 26,27/

The classic method for fabrication is to pour fine ceramic or metal powders in a metal container (usually called a "can"), evacuate and seal, apply pressure and heat for a set time in the pressure vessel. In the process, parts and materials are simultaneously compacted and sintered. Since the batches are pressed at very high pressures, near theoretical densities of the material are attained. This is not possible with other powder compaction processes. Similarly, the porosity is also eliminated. The dense, homogenous microstructure improves the performance of many types of products.

The automobile industry has been involved in the development of gas-turbine engines, wherein the fuel efficiency is maximized by operating the engine at higher temperatures. This would require a high-temperature ceramic such as silicon nitride or silicon carbide for the hot section of the engine. The Ford Motor Company has been actively involved in the development of both hot isostatic pressing and injection moulding of silicon nitride and silicon carbide. 28/ GTE Sylvania has also developed a high-temperature ceramic heat exchanger using a magnesium alumina silicate composition (cordierites) which can operate around 1,370°C. 29/ This material has been used in high-temperature process furnaces for the metal and ceramic industries.

It is of significant interest to note that this technology of hot isostatic pressing is also extensively used in powder metallurgy (PM) for developing new nickel-based alloys for high temperature use. The equipment, a hot isostatic press, is commercially available through ASEA Powdermet, a joint venture of the ASEA Group, Vasteras, Sweden, and two of its subsidiaries, Surahammars Bruks AB and Stal Laul Turbin AB.

Applications of high-temperature ceramics

High-temperature strength, resistance to thermal shock, corrosion and fatigue, and other properties of silicon nitride (Si_3N_4), silicon carbide (SiC) and SiALON families of ceramic materials currently make them attractive for application in diesel, stirling and gas-turbine engines. The advantages for the application of such ceramics to heat engines are as follows:

1. An increase in the turbine inlet temperature, which results in a lower fuel-comsumption and high power density

2. An increase in the reliability and a decrease in maintenance

3. An increase in corrosion resistance and in the temperature-intake capability of the engine

4. A reduced dependence on foreign fuel, which is a strategic benefit

5. A reduced dependence on strategic materials, such as cobalt, chromium and nickel, for countries dependent on foreign strategic materials.

The potential energy savings and the use of abundant raw materials (silicon, silica, sand) are particularly important for the industrialized developed countries. For these reasons, considerable time, money and effort have been expended towards the development of such high-temperature ceramics.

New polycrystalline high-temperature ceramics are also beginning to play an ever increasing role in high performance batteries, which are being designed for energy storage in utility load-levelling systems and as power sources for traction applications. 30,31/ Ion conducting ceramics, such as Beta-alumina, serve as solid electrolyte and separate and permit electro-chemical reactions between anodic and cathodic reactants. Rare earth perovskite, such as $YCrO_3$, mixed with transition metal oxides, are remarkable ceramics, having diverse magnetic, electrical and catalytic properties. Their potential applications are as electrodes for magnetohydrodynamic (MHD) power-generation and as catalysts for high-temperature catalytic combusion. 32,33/

In the last decade, a number of semi-conducting ceramic oxides such as Nb-doped $BaTiO_3$ have been identified, which serve as essential components in the photo-assisted electrolytic decomposition of water to produce hydrogen fuel. 34,35/ Advantages associated with the use of hydrogen fuel is that the source of hydrogen in the form of water is limitless and readily accessible: H_2 fuel may be readily stored, shipped and burned to produce heat or power vehicles and, in conjunction with fuel cells, to generate electricity efficiently without pollution.

These brief references indicate interesting prospects for high-temperature ceramics in various areas of energy production and conversion.

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References

1. Rustum Roy, "New ceramic materials produced by novel processing techniques", Powder Metallurgy International, v. 6, no. 1 (1974).
2. Della M. Roy et al., "EDS rapid solidification process application to specialized materials", final report, U.S. Bureau of Mines Contract No. G0155191, 15 November 1980.
3. Martin H. Stanczyk et al., "Comminution by the attrition grinding process", U.S. Department of the Interior, Bureau of Mines Bulletin, No. 670 (1980).
4. S. Yajima, "Development of ceramics, especially silicon carbide fibers from organosilicon polymers by heat treatment", Philophical Transaction, Royal Society of London, A 294 (1980), pp. 419-426.
5. S. Yasegawa, S. Yagima et al., "Synthesis of continuous silicon carbide fibre", Journal of Materials Science, v. 15 (1980), pp. 720-728.
6. S. Yagima et al., "Method of producing organosilicon high molecular weight compounds having silicon and carbon as main skeleton components", U.S. Patent No. 4,052,430.
7. R. W. Rice, "Preparation of turbine and related ceramics by polymer pyrolysis", Ceramic Gas Turbine Engine Demonstration Program, Metals and Ceramics Information Center, report 78, no. 36 (1978), pp. 633-640.
8. S. Yagima et al., "SiC and Si_3N_4 sintered bodies with new borodiphenylsiloxane polymers as binders", Nature, v. 266, no. 5602 (1977), pp. 522-524.
9. K. S. Mazkiyasni et al., "Characterization of organo-silicon infiltrated porous reaction sintered Si_3N_4", Journal of the American Chemical Society, v. 61, no. 504 (1978), pp. 11-12.
10. Robert West et al., "Polysilastyrene: phenylmethylsilane-dimethylsilane copolymers as precursors to silicon carbide", American Ceramic Society Bulletin, v. 62, no. 8 (1983), pp. 899-903.
11. R. R. Rowlands, "A review of the slip casting process", American Ceramic Society Bulletin, v. 45, no. 1 (1966), pp. 16-19.
12. S. G. Whiteway et al., "Slip casting magnesia", American Ceramic Society Bulletin, v. 40, no. 7 (1961), pp. 432-438.
13. Willard E. Hauth, III. et al., "Slip casting of tungsten shapes", American Ceramic Society Bulletin, v. 58, no. 2 (1979), pp. 179-183.
14. Robert M. Williams et al., "Slip casting of silicon shapes and their nitriding", American Ceramic Society Bulletin, v. 62, no. 5 (1983), pp. 607-619.
15. Mir Akbar Ali, "Development of tin oxide crucibles for melting optical glasses", U.S. Bureau of Mines Contract No. J0123056, 1981-present.
16. "Process and apparatus for the production of sparking plug insulators", U.S. Patent No. 2,305,877, 1962.

17. "Method of Injection Molding Ceramic Bodies Using Thermoplastic Binder", US Patent No. 2,434,271, 1948.

18. "Method of Molding Ceramic Articles", U.S. Patent No. 2,446,872.

19. "Molding of Ceramics", US Patent No. 2,694,245.

20. "Ceramic and Method of Making Same", U.S. Patent No. 2,564,859.

21. "Method of Molding Nonmetallic Powders", U.S. Patent No. 2,593,507.

22. Karl Schwartzwalder, "Injection molding of ceramic materials", American Ceramic Society Bulletin, vol. 28, no. 11 (1969), pp. 495-461.

23. John J. Burke et al., "Ceramics for High Performance Applications - I and II", Proceedings of the 5th Army Materials Technical Conference, Massachusetts, Brook Hill Publishing Co., (1978).

24. "Ceramics for Turbine Engine Applications", Agard Conference Proceedings No. 276, (London, Technical Editing and Reproduction Ltd., 1980).

25. Mir Akbar Ali, "Injection Molded Aluminum Oxide Components", In-House Project, Glass and Ceramics International, Inc., Lomita, California.

26. Tetsuo Yamada et al., "Densification of Si_3N_4 by high pressure hot pressing", American Ceramic Society Bulletin, vol. 60, no. 12 (1981), pp. 1281-1283, 1288.

27. T. Yamada, "Fabrication of Si_3N_4 by hot isostatic pressing", American Ceramic Society Bulletin, vol. 50, no. 11 (1981), pp. 225-228.

28. W. Trela, "Status of the Ford Program to Evaluate Ceramics for Stator Application in Automative Gas Turbine Engines". DOE. Conference of the 5th International Symposium on Automotive Propulsion Systems. April (1980).

29. Gordon C. Fay, "Development and Potential in the ceramic industry of the high-temperature ceramic recuperator body", American Ceramic Society Bulletin, vol. 62, no. 9 (1983), pp. 1036-1044.

30. "Research on electrodes and electrolytes for the Ford sodium-sulfur battery", Final Report, National Science Foundation Contract No. NSF-C-805, 1978.

31. "Development of sodium-sulfur batteries for utility applications", prepared for Electric Power Research Institute (EPRI), EPRI EM-683, May, 1978.

32. V. G. Gordon et al., Oxydes Refractaires pour Filieres Energetiques de Haute Temperature, Odeillo, France, 1977.

33. H. U. Anderson et al., The Rare Earths in Modern Science and Technology, (New York, Plenum Press, 1978).

34. T. Nehat Veziroglu, Proceedings of Hydrogen Economy Miami Energy Conference, Miami Beach, Florida (New York, Plenum Press, 1974).

35. M. S. Wright et al., Journal of the American Chemical Society, vol. 98 (1976), p. 2774.

NEW PROCESSING TECHNOLOGY IN TRADITIONAL CERAMIC INDUSTRIES *

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Ceramic raw materials

Ceramic raw materials belong to the group of non-metallic raw materials, though some of them can be used in the production of metals such as aluminium. Based upon their behaviour at 20°C, ceramic raw materials are classified into two main groups: plastic raw materials and non-plastic raw materials.

Plastic raw materials. The most important plastic raw material for ceramic production is the mineral kaolinite (Al_2O_3-SiO_2-$2H_2O$). Plastic raw materials form plastic paste when mixed with a proper amount of water. From this paste, various semi-products can be formed. De-watering of plastic raw materials during drying creates a change in volume, called drying shrinkage, and increases the strength of semi-products. Plastic raw materials are prone to cracking during drying. Semi-products lose their plastic deformation ability and become fragile. The strength of semi-products increases during firing. The first volume increase, due to thermal expansion, is followed by a volume reduction, called firing shrinkage. The porosity usually decreases and bulk density increases with the increasing firing temperature.

The plastic raw materials used in ceramics have their origin in the hydro-thermal decomposition of parent rocks, mainly feldspar. The products of decomposition either remained at their original places (primary raw material deposits) or were transported and sedimented in more or less distant places (secondary raw material deposits). The primary deposits are known to be of higher purity than the secondary ones. The products of hydro-thermal decomposition, i.e. quartz and kaolinite, sometimes contain traces of the parent rocks.

Contamination of plastic raw materials occurred during the movement to secondary deposits. The least contaminated clays are used for the production of non-vitrified light-coloured porcelain or sanitary ware products, or for the production of refractories. Depending on the degree of contamination, the more contaminated clays are used for the production of stoneware, bricks, or for other ceramic products for which colour is not important. In addition to the degree of contamination, primary and secondary plastic raw materials also differ in the size of clay particles. Primary raw materials are usually more coarse and, therefore, are also of lower plasticity and lower strength after drying and firing. They usually vitrify at higher temperatures.

Non-plastic raw materials. Non-plastic raw materials are classified into two main groups according to their behaviour during firing: grogs and fluxes. Mixing plastic raw materials with non-plastic ones lessens the plasticity, drying shrinkage and cracking during drying and firing.

Grog reduces or sometimes eliminates drying and firing shrinkage of plastic raw materials. In some cases, it can even cause the expansion of products, e.g. if quartz is used as grog due to its α-β modification transformation. This effect is important in the production of silica. The most frequently used grog is quartz (SiO_2), ground reject of fired products, various types of shales including high

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alumina, natural high-alumina materials, such as sillimanite (Al_2SiO_5), kyanite (Al_2SiO_5) and some special grog, such as corundum (α- Al_2O_3), silicon carbide (SiC) and zirconium silicate (ZrO_2 - SiO_2). A higher portion of grog in a body forms the skeleton of semi-products and products and determines the properties of products to a considerable extent.

Fluxes, during firing, function in a body as a grog until their fluxing effect, which lowers the temperature of sintering, sets in. They reduce the absorption and increase the strength of products. Traditional fluxes are mainly orthoclase and microcline (K_2O-Al_2O_3-6 SiO_2), dolomite (CaMg)CO_3), cryolite (Na_3AlF_6) and witherite or natural barium carbonate ($BaCO_3$). The non-traditional fluxes, such as albite (Na_2O-Al_2O_3-6 SiO_2), tuffs, tuffites, nephelines (K_2O-3 Na_2O-4 Al_2O_3-8 SiO_2), nepheline-syenites, phonolites, perlites, basalts, calcites ($CaCO_3$), marls, plagioclase, feldspars and magnesium raw materials are used increasingly. Industrial wastes and their concentrates, ground glass, slags and light ashes, are also used as non-traditional fluxes.

Some developing countries have no reserves of ceramic raw materials with sufficient plasticity. Organic or inorganic plasticizers are successfully applied together with fine grinding of some constituents and with new shaping methods.

Development of technologies

Manufacture of structural ceramics

Bricks

The favourable properties of ceramic materials in comparison with those of other building materials, especially for the construction of residences, have helped the brick industry to gain a good position in national economies of several countries and have contributed to the availability of low-cost housing during previous decades. Decorative bricks, used frequently for constructing fences and for decorating gardens, have also gained popularity. The contemporary production of roofing tiles is characterized by the development of new shapes and glazed tiles, resulting in mass reduction and improved aesthetic qualities. The production of drainage pipes is decreasing at present. Plastic pipes, which are easier to lay, are produced in only some developing countries. The raw materials are usually heterogeneous, relatively impure red-burning natural clays, sometimes combined with sand or ash. No burnt grog is used in the mixture. If necessary, siliceous sand can be added.

The feasible level of mechanization depends mainly on available capital, market potentiality and labour costs. Capital expenditures and labour productivity grow simultaneously with the level of mechanization. Charcoal heaps, down-draught or chamber kilns are used by cottage and small-scale industries for firing bricks, while production plants of higher capacity usually use Hoffmann and tunnel kilns. Firing temperature varies from 900°C to 1150°C, depending on the type of clay used.

The anticipated technological trends in the manufacture of bricks are:

- increasing production of hollow blocks, accelerating the construction and improving the thermal insulating properties of brickwork
- production of glazed roofing tiles
- new shapes of roofing tiles with reduced mass
- artificial aging of the clay instead of natural aging
- waste-heat utilization from kilns in driers, sometimes open-air drying to reduce energy consumption

- substitution of tunnel kilns for intermittent kilns in production plants with higher capacities
- construction of counter-current tunnel kilns in which two lines of kiln cars move in opposite directions. (The heat from cooled bricks is transferred to those heated in the other line, and specific energy consumption is lowered considerably.)
- waste-heat utilization, e.g. by joining periodical kilns for preheating bricks
- application of stain and wax pastes in order to improve product appearance
- production of clay floor tiles and facing tiles as a complementary product in brickmaking plants, vastly improving their entrepreneurial economy.
- application of pulverized coal as a substitute for gas and oil.

Stoneware pipes

Stoneware pipes are produced as salt-glazed, earthen-glazed, unglazed or glazed (on the internal surface only). The raw materials used are: vitrifying clays with low shrinkage and grog, such as fired shales, ground stoneware reject, quartz sand or a fine grain by-product of kaolin washing that can also act as a flux if a higher portion of parent feldspar rocks is present.

Stoneware pipes are manufactured either by semi-dry processing or wet processing. Pipes of diameters up to 300 mm are shaped either on vertical or horizontal worm de-airing presses. The type of presses depends on production capacity and assortment. Horizontal presses have higher output and usability for diameters up to about 300 mm. The moisture content of the green body for horizontally extruded pipes is usually lower, with 16 per cent as a maximum. The pipes with diameters above 300 mm are extruded on vertical worm de-airing presses. These presses use a higher relative moisture content of the clay, usually 17 per cent to 18 per cent. Bend pipes, angle pipes, breeches pieces and some other accessories are pressed on a specially adapted horizontal de-airing worm press. Some special fittings, produced in small amounts, are manufactured manually by bonding segments, cut according to templets.

Internal glazing is done either during extrusion by spraying the glaze on the internal surface of pipes or after drying by special glazing equipment that is inserted into the pipe and sprays the glaze on its internal surface. Complete glazing is done by dipping the pipes into a tank filled with the glaze slip. Before glazing, the edges of pipes are dipped into melted paraffin to keep them unglazed for firing. Glazing by salt is done by inserting the cooking salt (industrial salt) into the kiln at maximum temperature. The salt is decomposed in the kiln temperature. The components of decomposition are combined with water vapour from combustion products and form hydrochloric acid (HCl) and sodium oxide (Na_2O) that react with the body of pipes and form the glaze. The Seger formula of typical salt glaze - $1.0\ Na_2O-0.67\ Al_2O_3-3.33\ SiO_2$ - determines the necessary 3:1 ratio of $SiO_2:Al_2O_3$. Apart from this condition, the minimum temperature for salt glaze formation is 1120°C. Improvement of the surface and appearance of the glaze can be achieved by the addition of up to 10 per cent of borax ($Na_2B_4O_7-10\ H_2O$).

Green pipes are dried in chamber or channel driers by waste heat from kilns and usually by an auxiliary steam heater. Uniform drying is important to prevent bending of pipes. Open-air drying can be applied in productions with lower capacity in order to save energy in countries with warmer climates. The firing of stoneware goods has been done mainly in chamber and Hoffmann kilns. In modern production plants, depending on the market potentiality, shuttle kilns or tunnel kilns are used for firing stoneware. Firing temperature ranges between 1150°C and 1280°C.

The anticipated technological trends in the manufacture of stoneware pipes are:

- production of socketless pipes; special couplings are used while laying these pipes
- firing of socketless unglazed or inside-glazed pipes in kilns with a sloping floor. (The pipes roll slowly through the kiln. The firing cycle can be shortened by up to 1 hour with parallel reject reduction and very low specific consumption.)
- lowering of firing temperatures through body compositions
- waste-heat utilization, e.g. in joint periodical kilns
- production of other ceramics in stoneware production plants, widening the assortment and making the production flexible in meeting market requirements. (Numerous other products, such as cable ducts; decorative ceramics; clay floor tiles; facing tiles; non-fired refractories with hydraulic, chemical or ceramic bond; siliceous fireclay and chemical stoneware can be produced parallel with stoneware pipes.)

Clay floor tiles

Dense, vitrified tiles the colour of natural clays are frost- and erosion-resistant. They are used for exterior tilings of balconies, pavements, squares, terraces, garages and workshop floors, but generally not in housing interiors due to their rough surface. They are mainly produced from vitrifying clays, either by extrusion by worm de-airing presses or by pressing by hydraulic presses from semi-dry mixture. Clay floor tiles can be manufactured in brick-making, stoneware or fireclay production plants. Their production requires simple manufacturing equipment and is suitable for developing countries. Firing temperature, depending on raw materials, varies from 1000°C to 1200°C.

The anticipated technological trends in the manufacture of clay floor tiles are:

- further reduction of specific energy consumption, either by use of raw materials with low vitrifying temperature or by use of non-traditional fluxes
- balanced application of fine-ground fluxes in view of total energy consumption. (Fine grinding and mixing with the clay, which is indispensable, is an energy-demanding process.)
- reduction of the thickness of tiles
- production of clay floor tiles as a supplement product in brick-making, stoneware or fireclay production plants, improving the economy of production with regard to a more favourable selling price per kg. (Its introduction requires no or negligible additional investment.)
- production of relief tiles that are interchangeable with facing tiles
- bigger dimensions of tiles
- extrusion in pairs, quadrangles, etc. up to dodecagons that are split into individual tiles after firing.

Facing tiles for exterior applications

Dense, vitrified tiles are used for exterior tiling of house-walls or their parts, slaughter-houses, public buildings, comfort stations, etc. They are produced from vitrifying clays that are either the colour of natural clay, unglazed or salt glazed, with glazed, coloured engobes. Production of facing tiles is simpler than that of wall tiles and can be done in stoneware production plants, sometimes in brick-making plants or in refractories production, improving the economy of these plants. The tiles are either extruded by worm de-airing presses (coarse-ground raw materials) or pressed from semi-dry mixture on hydraulic presses (fine-ground raw materials).

The anticipated technological trends in the manufacture of facing tiles are:

- production of relief tiles for application in architecture
- firing of tiles in single-layer, multi-passage kilns or in conveyor kilns with low specific consumption and a short firing cycle (1 hour or even less)
- greater economy of stoneware, brick-making or refractory production plants by parallel production with clay floor tiles
- bigger dimensions
- parallel production of artistic ceramics.

Wall tiles

Wall tiles are produced from different raw materials: kaolinite, quartz, feldspar and limestone. Kaolinitic bodies, used originally for wall tiles, have two main disadvantages. In addition to a high firing temperature. they show high firing shrinkage, e.g. a small difference in firing temperature causes a great difference in product dimensions. The body compositions presently used, such as lime-siliceous, undergo mininum shrinkage between 1000°C to 1060°C, and desirable physical and mechanical properties are reached by firing tiles at these temperatures. Calibration is therefore not necessary. Moreover, high thermal expansion of lime-siliceous body makes possible the use of low melting glazes with high quality finish for temperatures ranging between 960°C - 980°C. Lime-siliceous, magnesium-lime-siliceous or magniesum siliceous bodies are the most suitable compositions for earthenware production in developing countries because of the large availability of raw materials.

Glazing of wall tiles is done mainly by a waterfall of the glaze. This method shows the best results in the quality of final surface. Low profile, semi-muffled kilns or modern single-layer passage kilns substitute for muffled kilns used in the past.

The anticipated technological trends in the manufacture of wall tiles are:

- energy conservation by decreasing the water content in a slurry using efficient slurry plasticizers. (It is recommended that the minimum proportion of dry matter to water be 60:40. A 1 per cent decrease in the portion of water in a slurry production plant with an annual output of 1 million m^2 of tiles results in an energy saving of more than 720,000 MJ, i.e. 17,500 kg of fuel oil per year, which represents about 3 per cent energy conservation during drying.
- introduction of single firing, bringing about 40 per cent energy conservation. (This task is rather difficult due to high quality requirements of products. Wollastonite-type bodies are most suitable for single-firing production.)
- development of new decorating techniques and improved quality of glazes
- production of bigger tiles, sometimes of rectangular shape
- large variety of designs
- utilization of lower quality body raw materials and opaque glazes
- reduction of necessary kiln furniture during firing
- bisque firing of double-fired wall tiles in tunnel kilns, glost firing by fast-firing in single layer
- dwindling differences between wall and floor tiles as they are applied interchangeably.

Floor tiles

There are two types of ceramic floor tiles: unglazed (dense, fully vitrified, coloured or white) and glazed (vitrified or semi-porous, with opaque glazes). Unglazed floor tiles are produced with two basic types of body: porcelain and clay. Porcelain floor tiles are composed of kaolin or white firing kaolinitic clays, quartz, feldspar and dolomite or limestone. They are used for white floor tiles and those whose colour is developed by blending stains into the white clay, such as blue and grey. Clay floor tiles are composed of vitrified clays, whose properties can be regulated by adding quartz, feldspar or feldspar pegmatites. The firing temperature varies from 1120°C to 1280°C, depending on the body composition. Glazed floor tiles are produced either as double-fired or single-fired. Double-fired floor tiles are produced by the earthenware technology used for wall tiles. Single-fired tile technology is similar to that of facing tiles but with raw materials ground to the requested fineness. Firing temperature of single-fired tiles fluctuates usually between 1100°C and 1200°C. Bisque firing of double-fired tiles is done at temperatures ranging between 1050°C and 1200°C; glost firing ranges from 960°C to 1000°C. Production of glazed floor tiles is suitable for developing countries with frost-free climates, enabling wide application of floor tiles that can be produced easily in wall-tile-producing plants. Glazed floor tiles are applied interchangeably with wall tiles.

The anticipated technological trends in the manufacture of floor tiles are:

- increasing production of glazed floor tiles and decreasing production of unglazed ones
- bigger dimensions
- single-layer firing
- single-firing of glazed tiles
- large variety of designs of glazed tiles that are easy to decorate to meet market requirements
- opaque glazes enabling application of lower quality clays for glazed floor tiles
- parallel production of glazed floor tiles and wall tiles
- dwindling differences between glazed floor tiles and wall tiles in application.

Fireclay refractories

Fireclay refractories are the most common refractories, and they are usually the first type to be manufactured in developing countries. Medium- and low-grade fireclay refractories can be produced by equipment similar to that used for stoneware or even bricks. Steel and iron production and production of other industries are conditioned by the application of fireclay refractories.

Fireclay products are manufactured from refractory clays and grog (fired shales, fired kaolins and ground fireclay reject). There are two basic methods of body preparation: plastic process (soft-mud) and dry process. The soft-mud process uses a plastic component and grog ratio ranging from 40:60 to 80:20; the dry process uses a ratio ranging from 30:70 to 10:90.

Lowering firing temperatures cannot be used to achieve energy savings, since low-fired fireclays would lose their quality and refractoriness. Firing is done in tunnel or chamber kilns at a temperature ranging from 1250°C to 1450°C, depending on the type and quality of final product.

The anticipated technological trends in the manufacture of fireclay refractories are:

- the use of non-fired grog in order to conserve energy
- application of shaped and unshaped non-fired ramming masses and refractory concretes. (Jointless lining made of these refractories is more corrosion-resistant since corrosion occurs mainly in joints. Non-fired refractories account for up to 40 per cent of total production in industrialized countries.)

- parallel manufacture of thermal insulators for high temperatures produced by the technology of combustible materials
- parallel production of refractory concretes
- parallel production of clay floor tiles and facing tiles to improve the economy of production.

Manufacture of utility ceramics

Dinnerware and decorative ceramics

A large variety of dinnerware and decorative ceramics can be produced, of which the most important types are stoneware, earthenware, vitreous china and porcelain. A large number of body compositions are used for dinnerware production. The use of highly variable raw materials enables production of utility ceramics in those countries that have deposits of plastic clays. Production can be done on a small scale, with minimum technological equipment, as well as in modern automated production plants, using single-firing and double-firing technology. Therefore, these ceramics are suitable for the majority of developing countries, from the least developed ones to traditional ceramic producers, depending on market potentiality.

Production of dinnerware and utility ceramics has passed through three stages of innovation in developed countries. The first one, after World War II, was characterized by substituting tunnel kilns firing gas for round down-draught kilns firing solid fuels. The second stage, in the late 1950s and early 1960s, introduced mechanization into production lines (mechanization of casting and shaping, introduction of glazing machines, grinding machines, sorting lines, decorating lines, etc.). The third stage of innovation in the 1970s was characterized by complex automation lines, including technological operations from shaping to glost firing.

The anticipated technological trends in the manufacture of dinnerware and decorative ceramics are:

- in porcelain manufacture, preparation of the blend in spray driers and isostatic pressing of flat pieces
- production of dinnerware and utility ceramics jointly with wall-tile manufacture. (Countries with little experience in ceramic production are recommended to start with the manufacture of earthenware dinnerware and, after sufficient experience and skill is gained, then follow with porcelain, stoneware and vitreous china, depending upon raw-material availability. Production of complete dinnerware sets brings about difficulties with regard to the variety of shapes and decorations. It is recommended that the production of complete sets commence after sufficient experience is gained in production of plates and cups.)
- similar problems are involved in decorating techniques. (Decalcomania (transfers) should be imported first and later production should start jointly with other types of decoration.)
- mechanization and automation to increase capital expenditures and productivity of labour, taking into consideration market requirements and variability of assortment produced.

Sanitary ware

Four types of sanitary ware are produced: earthenware, vitreous china, fireclay sanitary ware and stoneware. Principal sanitary ware products, such as wash-basins, bathroom fitments, closet bowls and sinks, are marketed both for household and communal utilities. Individual types of sanitary ware differ with respect to raw materials, firing technology (either single or double firing), absorption, bending strength, crushing strength and firing temperature. Vitreous china is the prevailing type of technology applied in sanitary ware manufacture. Sanitary ware is produced by slip casting, ranging from manual production for smaller capacities (which are labour-intensive, demand skilled workers, produce sophisticated shapes, permit assortment adaptability, and offer a high rate of return on investment with regard to low-capital expenditure on equipment) to automated casting lines in high-capacity production plants (which have a high labour productivity and better working conditions, but demand high capital-expenditures and higher energy consumption.

For vitreous china sanitary ware production, the single-firing technology is applied. Firing temperature in tunnel kilns ranges from 1200°C to 1300°C.

The anticipated technological trends in the manufacture of sanitary ware are:

. continued production of vitreous china sanitary ware due to lower investment costs and single-firing technology
. pressure casting of clay slip into synthetic moulds with high-quality castings, high durability of moulds, lower production costs and higher flexibility of production
. movement from high-capacity glazing lines to manual glazing or application of robots to meet market requirements for colour variability
. further energy savings during firing as a result of improved construction of kilns and equipment, waste-heat-utilization and decreased kiln furniture
. parallel production of artistic and utility ceramics, improving the economy of production.

Electroporcelain

Electroporcelain is classified according to low tension (used for voltages up to 440 v) and high tension (used above 440 v). Low-tension electroporcelain is unglazed for interior application and glazed for exterior applications. It can be produced jointly with sanitary ware or utility porcelain. Plastic clays, washed kaolins, talc, quartz and feldspar or pegmatite are used as raw materials.

High-tension electroporcelain is produced by more sophisticated technology from pure raw materials such as washed kaolin, high-quality clays, orthoclase and microcline, pegmatites, quartz sand or vein quartz and, if need be, flintstone or limestone and talc. Impurities, especially oxides of metals, lower the voltage resistance. Production of high-tension electroporcelain is possible only in countries with the necessary raw materials and market demand. Firing temperatures rang between 1380°C and 1420°C. Laboratories for testing final products to comply with relevant standards are indispensable in the production of high-tension insulators. These insulators are usually completed with steel fittings in production plants.

The anticipated technological trends in the manufacture of electroporcelain are:

. automated or mechanized shaping of mass-produced types.
. isostatic pressing of big, high-tension insulators from spray-dried clay
. drying big insulators with high-frequency electricity. (It is recommended to start with low-tension insulators and follow with high-tension insulators or with special ceramics after experience is gained.)

- firing in tunnel kilns in high capacity production plants and in shuttle and hood-type kilns in smaller plants
- completion of high-tension insulators with steel fittings in production plants
- parallel production of artistic ceramics, improving the economy of a plant.

Manufacture of other ceramic products

Silica

Silica is cheaper than high-alumina refractories but is only suitable for continuous kilns. It is produced with special qualities for individual applications, such as silica for coke ovens, metallurgical silica and silica for glass. Suitable raw materials are amorphous, cemented or, at least, fine-grained quartzites with a low content of alumina that acts as a strong fluxing agent. Its content in raw materials for high-quality silica must not exceed 1.0 per cent. The firing process must be carefully controlled due to the crystallographic changes of silica.

Silica is fired at temperatures ranging from 1400°C to 1500°C. Because of high requirements for raw material quality, technology adapted to the properties of raw materials and a usually limited market, silica production in developing countries is rare.

The anticipated technological trends in the manufacture of silica are:

- production of silica from grained quartzites
- parallel production of silica with high alumina and magnesite
- high-purity raw materials for products applicable to temperatures up to 1700°C
- application in glass, metallurgical and ceramic industries
- joint production of light-weight insulating silica bricks and silica in the same plant.

High-alumina refractories

High-alumina refractories contain a higher percentage of alumina than metakaolinite (Al_2O_3-2 SiO_2), i.e. higher than 45.9 per cent. Raw materials rich in alumina, such as pure alumina, vitrified alumina, sillimanite, andalusite, kyanite, bauxite or high-alumina synthetic grog, which is prepared from a mixture of kaolin and alumina, are used in the production of high-alumina refractories. Natural alumina raw materials, such as andalusite, bauxite, allophane, kyanite (disthene), diaspore, gibbsite and boehmite, frequently represent the possibility for a successful venture. Kaolinite, pure refractory clays or special inorganic or organic binding agents, such as phosphoric acid, alumophosphates and sulphite liquor, are used as binders.

High-alumina refractories are resistant to oxidizing and reduction atmospheres, some of them up to 1700°C, abrasion, slags and glass batch. Technology of high-alumina manufacture is similar to the manufacture of fireclay by the semi-dry method. The exact body composition and high-pressure pressing are characteristic of high-alumina production. The firing temperature depends on the type of product and varies from 1500°C to 1600°C. High-alumina can be produced also by casting from melted raw materials. Such technology, however, is more sophisticated, and it is not recommended to start with this technology.

With regard to the requirements for special raw materials and the applications for special purposes, production of high-alumina refractories in developing countries is possible after a higher level of development is reached.

The anticipated technological trends in the manufacture of high-alumina refractories are:

- application of high-alumina refractories as non-fired and non-shaped plastic and ramming masses and refractory concretes, monolithic linings of kilns, furnaces and other heating aggregates
- utilization of natural, upgraded high-alumina raw materials
- production of high-alumina refractories parallel with magnesite or silica refractories
- precise dimensions of final products.

Corundum materials

Corundum materials represent a special group of high-alumina products, with more than 80 per cent of alumina content. High resistance to oxidizing and reduction atmospheres up to 1900°C, abrasion, slags and glass batch is characteristic of corundum refractories. Electro-melted alumina or natural corundum, kaolins or refractory clays are used as raw materials, together with either chemical or ceramic binders. Corundum products are made either by isostatic or hot pressing and are fired at temperatures ranging from 1600°C to 1700°C. They are also manufactured by casting from a melt.

The anticipated technological trends in the manufacture of corundum materials are:

- application of natural high-alumina raw materials
- use for special purposes, mainly spark-plugs and burner stones, once fireclay production is established in developing countries according to the market, which is usually limited.
- possible parallel production in fireclay production plants equipped for this purpose by shuttle kilns.

Basic refractories

Basic refractories are special refractories such as magnesite, chrome-magnesite, olivine and forsterite products. Raw-material requirements amount to dead-burnt magnesite clinker, chrome ore with a maximum Al_2O_3 content of 12 per cent, olivine rocks, and sulphite liquor as a bond. Firing temperature varies from 1550°C to 1700°C.

Basic refractories are highly resistant to basic slags and melted metals. They are applied in the production of non-ferrous metals, such as copper, brass, nickel alloys and aluminium alloys. Production of basic refractories in developing countries is possible when a relatively higher level of development is reached. The availability of raw materials and market demand are necessary prerequisites for basic refractories production. Basic refractories can be produced parallel with silica and high alumina. Purity of raw materials is indispensable for products applied in high temperatures.

Special refractories

The three most important examples of special refractories are: (1) graphite refractories (high thermal conductivity and high thermal shock- and chemical-resistance, except for oxidation), (2) silicon carbide bricks and shapes (high mechanical strength, resistance to spalling, good thermal conductivity, resistance to reduction and to mechanical abrasion), and (3) zircon refractories (uniform thermal expansion and good thermal shock-resistance, used for the aluminium and glass industry and for calcium phosphate production). Production of special refractories is rare in developing countries and only occurs in countries that have a developed ceramic production (especially fireclay and high-alumina), the relevant raw material and market requirements.

Thermal insulators

Thermal insulators are classified into three categories according to the maximum temperature of application: low-temperature, medium-temperature and high-temperature insulators. Low-temperature insulators are applicable for temperatures ranging between 600°C - 700°C, such as glass wool and slag wool. Medium-temperature insulators are applicable for temperatures up to 1200°C, such as vermiculite, expanded clay products, diatomite, perlites and insulating fireclays. The light weight of materials is frequently achieved by the addition of organic materials (sawdust, coal dust, granulated coke, peat, cork or other combustible materials) in the clay mixture in order to decrease the bulk density of the product since they are fired out during firing. The body is usually prepared by wet mixing to desirable plasticity, either manually or mechanically. Extrusion of rough pressings on worm presses, overpressing, drying and firing follows. Some fired products are calibrated. Production of medium-temperature insulators is suitable for developing countries because of the availability of raw materials. Moreover, these insulators can be produced in brickmaking plants, plants for refractories or stoneware products. High-temperature insulators are applicable for temperatures up to 1600°C and are manufactured by several processes using the following materials:

- combustible materials, used in a similar way as in the production of medium-temperature insulators.

- foam-building materials, such as soaps and sodium resinates. This method produces fine-pored refractory insulating bricks with fine spherical pores, low thermal conductivity and relatively high mechanical strength. Pores are made by inclusion of foam into the ceramic slurry (fireclay or high alumina, depending on temperature of application). Calibrating of burnt products is a condition for their successful use.

- bubble-creating materials, such as aluminium dust, peroxide of hydrogen H_2O_2 and calcites, in acid or alkali milieu. The gas produced by chemical reaction forms bubbles in the slip. After hardening, the porous body is achieved.

- hollow clay or corundum balls, bound either by a refractory clay or by a chemical bond.

- sublimating matters, such as naphtalene and polystyrene. They sublimate out of the body before product maturity is reached, creating regularly distributed pores.

- insulating ceramic fibres, produced either by air blowing to a stream of a melted refractory mixture or by a centrifugal effect. Insulating folies, mats, felt, blocks and special shapes are produced from ceramic fibres. They have excellent thermal insulation properties and can be used for furnaces and kiln insulation.

The production and development of refractory insulators depend upon the level of industrialization of a country and the requirements of industry. They are important for any energy conservation programme.

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UNIDO'S ACTIVITIES IN THE CERAMICS SECTOR

Niels Biering *

Few industrial sectors represent such a wide range of technologies and end-products and are as flexible in terms of adaptation to local needs and resource endowments as the ceramics industry, defined as the totality of the clay-based manufactures. As a consequence, virtually all countries are engaged in the production of ceramics and even the least developed among them are realizing their potential and are also gradually benefiting from the considerable contribution of this sector to the overall socio-economic development.

The role that UNIDO is requested to play in this development process is that of a promoter of technological innovation, a source of know-how and practical support for existing and emerging industries and a catalyst for self-sustained growth in those branches of the industry where the basic technology is already well mastered. As the following examples from the current UNIDO work programme will show, the services provided range from the provision of general information, by means of training and consultant missions, to the establishment of complete production units and research and development laboratories. Although simpler and more traditional technologies still dominate the overall picture, increasing attention is being devoted to the more advanced and sophisticated end of the technological spectrum.

Pottery making is an activity as old as the civilizations to which they belong, and in many parts of the world neither the designs of the products nor the techniques employed in their manufacture have changed much over the past centuries. While it is desirable to maintain and protect the cultural heritage represented by the traditional design, it is equally desirable to introduce technological improvements to the traditional potter's communities in order to protect and improve their future existence. In Bolivia, a UNIDO project, financed by the Voluntary Fund for the United Nations Decade for Women, is presently providing assistance to the pottery village of Huayculi in the Province of Cochabamba through means of a co-operative support-unit comprising a mechanized clay-preparation plant, electrical kilns and a training workshop intended to introduce hand-throwing techniques (so far not practiced by the women of the village) and slip-casting technology (allowing the addition of new mass-produced items to the traditional product range). Within the near future, it is expected that this co-operative support unit will contribute significantly to the viability of the 40-odd family workshops of the village. Similar projects are now under preparation in Costa Rica, Nepal and Tanzania.

From a geographical point of view, the introduction of brickfiring as a means of rendering the traditional, sun-dried clay blocks durable has not been as widespread as that of pottery making. However, the late arrival of this technique in some areas, for instance in Africa, is compensated by the efforts now undertaken to make fired bricks available even in remote rural areas. During recent years, UNIDO has advised some 20 African countries on the potential for domestic brick manufacture through means of raw material investigations, market studies, feasibility assessments and elaboration of technological proposals, in several cases leading to the establishment of mechanized brickworks with equipment financed

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either, as in the case of Lesotho, by bilateral loans obtained on the basis of UNIDO's preparatory work and continuing support commitment or, as in the case of Gambia, completely financed by UNIDO thanks to a special purpose contribution to the United Nations Industrial Development Fund (UNIDF) from the People's Republic of China. In Niger, an expert is presently advising on the efficient operation of a newly erected modern brickplant, while a project recently completed in Mozambique has led to the start of almost 100 artisanal brickmaking units attached to an equal number of communal villages.

The know-how and experience acquired through the manufacture of pottery and heavy clay products is a logical first step towards production technologies requiring higher grade raw materials, more mechanization and high firing temperatures. UNIDO is a strong promoter of such an organic growth of the ceramic sector. However, these industries, which include wall and floor tiles, dinnerware, sanitary ware, electrical insulators and refractories, not only require a higher level of technology but also a larger market and a size of investment that dictate careful preparatory investigations and studies.

Depending on the local expertise available, either a small or substantial amount of outside assistance is required for the successful implementation of ceramic projects, and UNIDO has often been called upon to provide authoritative and unbiased advice on the suitability of raw material, the market potential, the choice of technology and the financial viability in connection with such industrial investments.

As a matter of principle, technologies are developed on the basis of local raw materials, reducing to a minimum the need for imports. In addition to geological surveys, in which UNIDO also from time to time becomes involved, this requires careful technological evaluation of the available mineral resources: laboratory investigations and semi-industrial trials are carried out by UNIDO through contracts with high-level ceramic research institutes. In particular, the Czechoslovak Research Institute for Ceramics, Refractories and Raw Materials should be mentioned due to the close contact established with this institution through the UNIDO-Czechoslovakia Joint Programme for International Co-operation in the Field of Ceramics, Building Materials and Non-metallic Minerals Based Industries. By way of example, this Institute has carried out extensive investigations of raw materials in Suriname, in which technicians from Suriname also participated, leading to the elaboration of a glazed-tile project.

Some projects have been developed based on non-conventional raw materials, for instance in Cyprus where a tile body was proposed using dead burned bentonite in the absence of more suitable clays, or in Jamaica where a Hungarian technology for sintered floor tile production using red mud, a waste material from aluminium production, has yielded high-quality products.

In Yugoslavia, which used to import a major part of its ceramic raw materials, a large-scale UNIDO project is now bearing its fruits. A non-metallic minerals and ceramics department was recently established at the Serbian Institute for Technology of Nuclear and Other Mineral Raw Materials. Thanks to a well-equipped laboratory and pilot plant for minerals beneficiation, including a semi-industrial flotation plant and a high-intensity magnetic separator, technologies are now made available to the industry, allowing it to upgrade and use local kaolins, feldspar, sands, etc. as a replacement for hitherto imported materials. Although initially the establishment of a well-equipped ceramics laboratory is more costly both for the respective Government and for UNIDO than testing the materials abroad, it is, in the long run, a much more efficient way of promoting the growth of a ceramic industry based on domestic resources and national expertise.

Probably, the best example of a UNIDO project aiming at strengthening national self-sufficiency in the ceramic sector is a project in Sri Lanka that was initiated in 1983 and financed by a special purpose contribution to the UNIDF by the Federal Republic of Germany. The project is satisfying an old wish of the Ceylon Ceramics Corporation which, with more than ten production plants producing a full range of heavy clay and fine ceramics products, belongs to the most important ceramic manufacturers in Eastern South Asia. With UNIDO financing, a central research, development and quality control laboratory has been established and provided with a large amount of equipment, including an electron-scanning microscope and an X-ray diffractometer and spectrophotometer. The inauguration of this laboratory, scheduled for September 1984, will mark the beginning of a new era for the Sinhalese ceramic industry and the remainder of the project will be devoted to the introduction of the know-how and skills necessary to allow the national staff to make the fullest possible use of the facilities.

In addition to serving the existing production plants, it is the intention of UNIDO to also undertake advanced product development, inter alia, in the field of new ceramic materials, such as nitrides and carbides, thus making this the first UNIDO project giving greater attention to this area of front-line research. Judging from the increasing interest shown by the more advanced among the developing countries, other projects will soon enter into this field. A recent request from the Government of Romania for assistance in developing technologies for metal-oxide ceramic resistors to protect against transient overvoltages is a good indication of a trend now being formed.

Another trend that has emerged with ever-increasing clarity over the past few years is the imperative need to reduce the energy consumption of ceramic industries and to introduce modern concepts of energy management at plant level. In-plant training workshops have been organized by the UNIDO-Czechoslovakia Joint Programme, to focus on this subject, and through consultant missions to Brazil and India the scope for direct assistance to the ceramic industry in this respect has been explored. Several publications have been prepared by the Joint Programme that have exposed the possibilities for energy savings both through change of body compositions, firing conditions, other technological details and through modifications of the kilns and dryers themselves.

A description of UNIDO's involvement in the ceramic industry would not be complete without briefly touching upon the two major sectors of which it constitutes an important part, i.e., the non-metallic mineral-based industry and the building-materials industry. Both sectors, which to a large extent are overlapping, are enjoying high priority in most developing countries because of the enormous economic potential of the raw materials concerned and because of the key role played by the housing and construction sector (and with that the manufacture of building materials) in the socio-economic development process.

In its co-operation with developing countries, UNIDO attempts to see the industrial utilization of non-metallic minerals in this larger context and to promote an integrated exploitation of the resources available. Long-range planning enters into the picture in an effort to reserve high-grade raw materials for high-grade applications or, alternatively, to identify economic uses for low-grade materials otherwise categorized as wastes. By the same token, the use of building materials based on local clays or other domestic natural resources is promoted as an alternative to importation. In this way, the development of the ceramic industry and the related sectors serve as an example of good resource management intended to allow this sector to grow in a healthy way for many years to come.

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PUBLICATIONS

Publications available from UNIDO

The following are some recent UNIDO publications, listed in chronological order, that deal with the ceramics industry. Copies may be obtained free of charge on request from the Editor, UNIDO Newsletter, United Nations Industrial Development Organization, P. O. Box 300, A-1400 Vienna, Austrria. The language in which the publication is available is indicated.

"Simple Ceramic Manufacturing Equipment", UNIDO-Czechoslovakia Joint Programme, Vienna, Austria, 1981, 61 pages. UNIDO/IO.483. English.

"Clay Samples from Papua New Guinea: Technological Evaluation", Milan Grotte and Miroslav M. S. Stockert, Vienna, Austria, 1980, 33 pages. UNIDO/IO.342. English.

"Ceramic Glazes. Basic Information", Zdenek A. Engelthaler, Vienna, Austria, 1983, 26 pages. UNIDO/IO.563. English.

"Main Quality Factors of Tableware. Basic Information", C. Cermak, Zdenek A. Engelthaler, and Milan Nový, Vienna, Austria, 1983, 19 pages. UNIDO/IO.564. English.

"Manufacture of Laboratory Porcelain. Basic Information", Milan Nový and S. Sabata, Vienna, Austria, 1983, 20 pages. UNIDO/IO.566. English.

"Heat Diagnoses Made on Tunnel Kilns and on Belt Drier. Basic Information", Milan Nový, Vienna, Austria, 1984, 44 pages. UNIDO/IO.572. English.

Publications available from the UNIDO-Czechoslovakia Joint Programme for International Co-operation in the Field of Ceramics, Building Materials and Non-metallic Mineral-based Industries

The following is a list of some of the publications, listed in chronological order, that are available on request from the UNIDO-Czechoslovakia Joint Programme for International Co-operation in the Field of Ceramics, Building Materials and Non-metallic Mineral-based Industries, P.O. Box 211, Pilsen, Czechoslovakia.

"Non-metallic Raw Materials - Source of Energy Conservation", Z. A. Engelthaler, M. Grotte, J. Krejsa, L. Kuna, JP/21/79, 1979.

"Energy Saving Possibilities in Non-metallic Mineral-based Industries at Present and in the Long Run", Z. A. Engelthaler, M. Grotte and L. Kuna, JP/6/79, 1979.

"Other Non-metallic Raw Materials", M. Kuzvart, JP/14/79, 1979.

"Technological, Physical and Chemical Testing of Non-metallic Raw Materials", V. Tehník, JP/19/79, 1979.

"Specification of Limestone and Kaolin Properties for Their Use as Fillers for Plastics", J. Baburek, JP/58/80, 1980.

"Equipment for Laboratory Testing of Kaolin, Clays and Sands", M. Bares and J. Drevo, JP/61/80, 1980.

"Energy Conservation in Non-metallic Mineral-based Industries", J. Drevo, Z. A. Engelthaler, M. Grotte, L. Kuna, J. Lahovsky, JP/27/80, 1980.

"Silvering Suspensions for Electrotechnical Industry and Electronics", Z. A. Engelthaler, M. Grotte, E. Prihoda, JP/49/80, 1980.

"Stimulating of Thermal Processes in Silicate Industries", M. Nemecek, JP/46/80, 1980.

"Testing Institute and Plant Laboratories for Testing Non-metallic Raw Materials and Products", M. Bares, J. Drevo, B. Hatak, JP/81/81, 1981.

"Non-traditional Ceramic Raw Materials Enabling Savings in Energy", Z. A. Engelthaler, JP/78/81, 1981.

"Non-traditional Raw Materials, Source of Energy Conservation", Z. A. Engelthaler, JP/80/81, 1981.

"Ceramic Industry, Reducing the Energy Requirements in Technological Processes", Z. A. Engelthaler, JP/91/81, 1981.

"General Consideration on Energy Consumption in Silicate Industry", L. Kuna, JP/89/81, 1981.

"Non-metallics - Their Contribution to Energy Conservation", J. Baburek, JP/125/82, 1982.

"Energy Savings in Composing Ceramic Bodies", Z. A. Engelthaler, JP/128/82, 1982.

"Energy and Materials Flows in the Manufacture of Selected Ceramic Products", J. Müller, JP/127/82, 1982.

Publications available from The American Ceramic Society Book Service

The following is a list of only a few of the publications available from The American Ceramic Society Book Service, 65 Ceramic Drive, Columbus, Ohio 43214, United States of America.

Loran S. O'Brannon, Dictionary of Ceramic Science and Technology, Plenum, 1984, 330 pages. (Non-member $45/Member $36)

Clifton G. Bergeron and Subhash H. Risbud, Introduction to Phase Equilibria in Ceramic Systems, University of Illinois, 1984, 275 pages. (Non-member $30/Member $25/Student $20)

Phase Diagrams for Ceramists, Cumulative Index, compiled by the U.S. National Bureau of Standards, 1984, 96 pages. (Non-member $15/Member $10)

Additives and Interfaces in Electronic Ceramics, vo. 7, 29 papers from the Grain Boundaries and Interfaces in Ceramics Symposium held at the American Ceramic Society's 1982 Annual Meeting, 1984, 350 pages. (Non-member $45/Member $35)

Forming of Ceramics, vo. 9, 30 high-technology papers presented at the American Ceramic Society's Conference on Forming, 1984, 300 pages. (Non-member $45/Member $35)

Ultrastructure Processing of Ceramics, Glasses and Composites, 42 papers presented at the 1983 International Conference on Ultrastructure Processing of Ceramics, Glasses, and Composites at the University of Florida, 1984, 575 pages. (Non-member $70/Member $60)

David W. Richerson, Modern Ceramic Engineering, Marcel Dekker, 1982, 392 pages. (Non-member $55/Member $44)

MEETINGS

From Clay to Ceramics: An Exercise in Physics, Technology and Art, 26 May 1984: Physics, uses and the origin of life with clay, ceramics in prehistory, new visions in art. For more details write to the American Association for the Advancement of Science, AAAS Meetings Department, Box 5, 1101 Vermont Avenue NW, Washington, D.C. 20005, United States of America.

1984 Tecnargilla: 9th International Machinery and Technology Exhibition for Ceramic Industry, Rimini, Italy, 2-7 October 1984. For further information and news about Tecnargilla, write Ente Autonomo Fiera Di Rimini, Via della Fiera, 23-1, 47037 Rimini, Italy. The schedule of meetings is as follows: 2-4 October, Present Situation and Evolutionary Trends in the Tableware and Sanitaryware Industries, 5 October, Meeting of the Italian Association of Clay Production Industrialists, and 6 October, Technician's Day, "Quality Assurance in the Ceramic Tile Industry".

2nd International Conference on Joining of Ceramics Glass and Metal, Bad Nauheim, Federal Republic of Germany, 27-29 March 1985. For details write to Deutsche Keramische Gesellschaft eV, Postfach 1226, D-5340 Bad Honnef 1, The Federal Republic of Germany.

World Congress on Non-Metallic Minerals. The Yugoslav Union of Engineers and Technicians, Miners, Geologists and Metallurgists, in co-operation with Industrial Minerals, part of the Metal Bulletin Journals Ltd. of London and New York, are organizing the I World Congress on Non-Metallic Minerals. The Congress will be held in the modern Belgrade Sava Centar, 15-19 April 1985. For more details, write to the I World Congress on Non-Metallic Minerals, Sava Centar, Belgrade, Yugoslavia.

8th Symposium on Special Ceramics, London, United Kingdom, December 1985. For details write to Assistant Secretary, British Ceramic Society, Shelton House, Stoke Road, Shelton, Stoke-on-Trent, ST4 2DR, UK.

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Readers' comments

We should appreciate it if readers could take the time to tell us in this space what they think of the second issue of Advances in Materials Technology: Monitor. Comments on the usefulness of the information and the way it has been organized will help us in preparing future issues of the Monitor. We thank you for your co-operation and look forward to hearing from you.