Raw Materials

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THE RAW MATERIAL BASE of the ceramics industry is extensive and ranges from mineral products and ores to highly refined chemicals. The uses of these materials include applications in traditional industries such as building products, whitewares, and refractories as well as in newer high-technology industries such as electronics. Materials are selected for these applications mainly on the basis of price and availability while still being consistent with fitness for purpose criteria. These criteria relate to the achievement of market acceptable end product properties through the use of minimum cost high efficiency production processes. There is a clear pattern of national and international trading of a significant number of raw materials to the ceramics manufacturer but there is also a considerable amount of in-house materials sourcing and preliminary materials processing by the producer. The latter is particularly true in the building products sector, where in-house sourcing and processing is the norm, and in high-technology applications where some users favor the production of their ceramic materials from chemical precursors.

In all cases, companies are active in improving and updating their products and processes to match market requirements and in high-technology applications this is complemented by active and vigorous academic research.

This discussion provides an overview of the economically most significant materials in current use and at the same time indicates material technologies that are likely to emerge as commercially viable in the foreseeable future.

Selection of Ceramic Raw Materials Based on Product Applications

The raw materials used as constituents in ceramics all have their primary origin in nature. Some raw materials are incorporated into ceramic products in their natural form while others require treatment and processing prior to use. In general, raw materials for large-tonnage products (such as brick, concrete, refractories, and so on) receive little or no preliminary processing while those for low-tonnage ceramic products (such as ceramics used for electronic components, ceramic cutting tools, and optical glass) receive extensive beneficiation. This is a consequence of both economic considerations and property requirements. The trend today is toward additional processing of all raw materials, even for large-tonnage applications, because there are more restrictive and narrow specification requirements applied to the properties of ceramic products and because the best natural deposits are being gradually depleted.

Industrial and Residential Building Products (Ref 1–4)

In most countries of the world, naturally occurring clay minerals are processed into bricks, roof tiles, and drainage pipes by plastic forming of the raw material into greenware that is fired at 900 to 1100 °C (1650 to 2010 °F) in intermittent or tunnel kilns. End product properties are usually defined by local building regulations. In the case of bricks and tiles, there is a need to comply with building style trends and to produce products with an aesthetic appearance in terms of both color and surface texture. The European market for these clay products is very extensive (see Table 1). However, it is difficult to place a monetary value on the raw materials used because in almost every case the end user sources clay from an in-house deposit.

No two clay bodies are the same and indeed there are generally variations in quality, both physical and chemical, throughout the deposit. A typical clay reserve, inasmuch as any can be described as typical, contains an impure kaolinite as a major phase together with a range of other minerals (for example, silica, mica/illite, feldspar, dolomite, calcium sulfate, and calcium carbonate) in variable amounts. In addition, most building clays contain transition elements (for example, iron as pyrites, hematite, and so on) and frequently significant amounts of carbon and other organic matter from the partial degradation of vegetation trapped in the sedimentary clay during its geological formation. This complex mineral array must be processed into a consistent feedstock in order that today's modern high-efficiency automated brick, tile, or pipe plant can meet its production targets in terms of output, product properties, and overall manufacturing costs. The consistency of the clay feedstock is achieved by the controlled mining of clay from a pit that has been previously characterized chemically, mineralogically, and physically by a forward borehole drilling program. Extracted clay is subsequently stockpiled in layers in quantities that can approach a 6- to 12-month supply of raw material per plant requirements. The stockpile is layered horizontally and the material for operating the plant is then taken vertically to meet the ongoing plant demand.

Historically, most plants were operated with little, if any, product or process additives, although clay deposits were frequently chosen on the basis of the fired color and appearance imparted by some of the impurities. However, as the industry grew, a business in product and process additives slowly emerged. The most significant additives are processing aids such as lignosulfonates, which by acting either as flocculants, deflocculants, or wetting agents, improve clay workability and green strength, and additives such as colorants and antiscum compounds that improve product appearance. There are a significant number of proprietary systems on the market including:

- Body stains and whiteners, based on milled pyrolusite (manganese dioxide), milled hematite (iron oxide), milled chromite (iron chromite), calcium carbonate, zinc oxide, and titania
- Surface colors, which include naturally occurring and synthetic iron oxide pigments and zinc oxide pigments
- Antiscumming compounds, based on barium carbonate that fixes free sulfate in the green brick and minimizes the migration of calcium sulfate to the brick surface during drying

It is projected that the building products additives market will continue to grow as the industry undergoes cost, product design, and environmental pressures. Additives that can increase production rates, improve yields, reduce plant maintenance, meet styling trends set by the consumer and reduce or control sulfur dioxide emissions will be traded on an international basis.

Whiteware (Ref 5–13)

The whiteware sector comprises sanitaryware, wall and floor tiles, and tableware.

Production occurs throughout the world to suit local needs, using mainly locally available raw materials, although high-quality tableware and wall tiles are traded internationally. The raw materials for the industry fall into three distinct categories:

- Body materials
- Glaze materials
- Decoration and color systems

Typical formulations, key components, and physical properties of these three categories are shown in Table 2.

Body materials are chiefly based on white firing kaolinitic clays together with suitable fluxes required to vitrify the body on firing at temperatures in the range of 900 to 1300 °C (1650 to 2370 °F). All the materials are traded on a national and an international basis to major customers and each material is supplied according to agreed specifications that ensure its fitness for each specific application.

Glaze systems are based on glass forming systems, opacifiers (to impart opaqueness), and glaze colors. The glaze systems are carefully matched to conform to customer requirements such as:

- Methods of application
- Physical and chemical match to the body system
- Good durability in use and during cleaning/washing
- Low release of toxic elements into foodstuffs in the case of tableware
- Aesthetic appearance in terms of luster, flatness, and freedom from defects

Decoration and color systems can be applied underglaze, in-glaze, or on-glaze and as such must be chemically and physically compatible with the substrate and the glaze during high-temperature firing and also resistant to normal treatment by end users.

The supply of raw materials to this sector is a multimillion dollar business. The key components for body systems are china clay, ball clay, quartz, nepheline syenite, feldspars, bone ash, and synthetic fluxes. On the other hand, glass frits (prepared from lead, boron, and silica) and milled zircon opacifier are major glaze components. Zirconia is the basis for the zircon colors with synthetic spinels and sphenes adding to the color range.

Table 1 European heavy clay products production in 1988

	Clay brick			
	Solid and perforated		Hollow	
Country	m^3	ft^3	m^3	ft^3
Germany	6,177,000	218,100,000	1,639,000	57,880,000
Austria	2,065,000	72,930,000	...	...
Belgium	1,257,000	44,390,000	...	...
Denmark	86,000	3,040,000	...	...
Finland	215,000	7,590,000	...	...
England	2,840,000	100,300,000	...	...
Italy	3,320,000	117,200,000	9,630,000	340,000,000
Netherlands	95,000	3,350,000	...	...
France	685,000	24,200,000	2,281,000	80,550,000
Norway	4,981,000(a)	4,981,000(a)	...	...
Switzerland	1,069,000	37,750,000	...	...
Spain	1,792,000	63,280,000	8,444,000	298,200,000

(a) Pieces. (b) m^3. (c) ft^3. (d) tonne. (e) ton

Marketability of Raw Materials. The market for the above materials is optimistically only increasing slowly in the western world, but third-world countries offer potentially lucrative markets as their standard of living increases. Key factors that will affect the raw materials supplier are the technological changes taking place within the industry. These changes relate to cost, quality, and environmental pressures. The industry is addressing both cost and quality factors by adopting rapid and more automated fabrication techniques (for example, isopressing of spray dried body formulations for tableware and pressure slip casting for sanitaryware) and fast firing technologies while simultaneously attempting to control toxic elements such as lead and cadmium is becoming increasingly important.

Refractories (Ref 14–18)

The refractory business is very dependent on the global iron and steel industry and 50 to 60% of all refractories are supplied to this sector of the market. The remaining portion is used in the production of cement, glass, nonferrous metals, petrochemicals, and ceramic products. In the last two decades, there has been a marked decline in the usage of refractories worldwide by the iron and steel industry due to production cutbacks and dismantling of obsolete facilities and the introduction and consolidation of improved process methods such as basic oxygen steelmaking (BOS), high-powered electric arc furnaces (EAF), and continuous casting. The refractory industry has adapted to these changes by introducing new products with improved properties and longer service life. A clear example of the decline in refractories use is provided by the Japanese refractory industry that has declined from 2.4×10^6 to 1.8×10^6 tonnes (2.6×10^6 to 2.0×10^6 tons) in the period 1981 to 1986, while the Japanese steel output remained approximately constant at 1×10^8 tonnes (1.1×10^8 tons).

Refractory products are supplied to the user industries in the form of as-fired shapes, unfired shapes, and monolithics. There are clear trends toward the use of monolithic products for all applications and toward unfired shapes in the iron and steel industry.

The supply of raw materials to the refractory business has evolved from one that was dependent on locally available raw materials to one that is now dependent predominantly on internationally traded materials. There are some notable exceptions such as silica, dolomite (in Europe and the United States), low-quality clays, and pyrophyllite (in Japan), while some third-world countries can favor the use of low-quality indigenous materials over the optimum imported product in order to conserve foreign exchange.

The main refractory raw materials are listed in Table 3 in terms of typical properties, applications, and sources of supply. These include the materials that form the body of the product as well as the bond systems (both temporary and permanent) and minor additives. The major tonnage materials include not only standard minerals but also microstructurally designed products such as magnesia and relatively high priced, high-performance materials such as alumina, silicon carbide, and zirconia. Chammotte, bauxite, magnesia, and graphite contribute to a significant percentage of the overall refractory materials business, but the specific consumption of these materials (quoted for example as kg/tonne of steel) will continue to decline as end users demand improved performance and only a strong expansion in customers activity will prevent a downturn in overall supply requirements. It could be inferred that growth opportunities exist for materials such as silicon carbide and zirconia and, while there seems little doubt that these materials will be used more widely, growth may well be limited by astute refractory product design which, by the use of liners and/or coatings, could limit high priced materials to key contact areas. Materials substitution within the industry will thus occur on a value in service basis.

Bonding systems include temporary bonds such as lignosulfates for fired products and permanent bonds such as resins in carbon bonded products and calcium aluminate cements in refractory castables. While body materials have improved in terms of reproducibility and quality, there have been advances in the use of novel bonding systems and this area is forecast to offer opportunities for future development.

The market for refractory insulation materials based on ceramic fiber has increased rapidly in the last two decades as the main

Facing brick		Materials for horizontal structures		Roofing tile	
m^3	ft^3	m^2	ft^2	m^2	ft^2
1,699,000	60,000,000	64,000(b)	2,300,000(c)	25,267,000(b)	892,300,000(c)
...	...	890,000	9,600,000	728,000	7,830,000
666,000	23,500,000	...	...	...	...
382,000	13,500,000	...	...	22,268,000(a)	22,268,000(a)
216,000	7,630,000	...	...	...	...
5,986,000	211,400,000	...	...	...	...
...	...	89,700,000	965,000,000	31,200,000	336,000,000
1,620,000	57,210,000	...	...	45,500,000(a)	45,500,000(a)
...	...	73,000(d)	80,000(e)	2,030,000(d)	2,230,000(e)
19,418,000(a)	19,418,000(a)	...	...	...	...
67,000	2,400,000	...	...	146,053,000(a)	146,053,000(a)
672,000	23,700,000	1,250,000(d)	1,380,000(e)	650,000(d)	720,000(e)

refractory users strive to save energy in their processes and reduce costs. The most used fiber is based on high-quality clay, but fibers based on alumina and zirconia also have widespread applications.

The effect of refractory materials on the environment cannot be overlooked. Products that are hazardous to the health of process workers and customers and that result in disposal problems are already coming under close scrutiny. Three notable examples of hazardous refractory materials are:

- Chrome ore; substitute materials are being actively sought and evaluated
- Baddeleyite, a naturally occurring zirconia, contains radioactive isotopes of zirconium, which make this material and products based on it a registered hazardous material in the United States
- Organic resins, used for making unfired shaped carbon containing refractories, are being closely monitored in terms of product handling and burnout in customer plants

The raw materials suppliers will be under continued pressure, therefore, to control costs, quality, and service. All efforts will be made to reduce the specific energy consumption, to reduce the level of deleterious impurities, and to optimize microstructural properties. Opportunities exist for the development of new materials that can withstand the operating environment and for novel bonding that can improve product quality and/or reduce production costs through improved processing. Key properties for which improvements are being sought are corrosion resistance, oxidation resistance, and thermal shock resistance.

Advanced Ceramics (Ref 19–30)

Whereas the three sectors previously discussed represent traditional ceramics markets that have slow growth or declining markets, the advanced ceramic sector represents new markets for ceramics, some of which have shown phenomenal growth over the last few decades. The major market for state-of-the-art ceramics has been and will continue to be in electronics, but vigorous worldwide research and development programs are continuously searching for new applications and identifying ways of improving ceramic properties such that new markets can be accessed.

Advanced ceramics are produced in Japan, the United States, and Western Europe. The raw materials used in the industry are traded on an international basis, principally as powders, but there is also a significant amount of in-house processing. The estimated United States market for ceramic powders by market and product type for the period 1989 to 1995 is listed in Table 4. While the absolute value of this market is difficult to quantify because of the in-house processing and trends in some markets to use less raw material per component, there is no doubt that both the electronics market and the supply of oxides to this area are dominant. Furthermore, these mar-

Table 2 Composition and physical properties of raw materials used for whiteware applications

	Composition			
Raw material	Frit materials	Raw glaze materials	Constituents	Typical properties of fired ware
Body materials				
Bone china	...	...	Bone ash, china clay, quartz, feldspars	Pure white, translucent, high strength, zero water absorption
Porcelain	...	...	China clay, feldspars, quartz	Pure, bluish, or off white, translucent, high strength, zero water absorption
Hotelware	...	...	Quartz, ball clay, china clay, feldspars	Off white, good physical and chemical durability, zero water absorption
Earthenware	...	...	Quartz/flint, china clay, ball clay, feldspars	Ivory to pure white, lower strength, water absorption 4 to 8%
Sanitaryware	...	...	China clay, ball clay, fire clay, quartz, feldspars, nepheline syenite	...
Wall/floor tiles	...	...	Ball clay, fire clay, quartz, feldspars, limestone	...
Glazes	<1150 °C (2100 °F): Quartz, sodium borate, boric acid, limestone, feldspars, china clay, lead oxides, zircon, zinc oxide, alkali metal, carbonates, and nitrates	...	...	Transparent to opaque, colored or colorless, glossy, matte, vellum, or textured
Pigments	...	>1150 °C (2100 °F): Feldspars, quartz, clays, nepheline syenite, limestone, dolomite, zinc oxide, zircon	...	Transparent to opaque, colored or colorless, glossy, matte, vellum or texured
Zircon-based	...	...	Zirconia, quartz	...
Spinel-based or oxide colorants	...	...	Iron, chromium, zinc, nickel, copper oxides or compounds	...
Sphene-based	...	...	Quartz, limestone, tin oxide	...

Table 3 Composition, applications, and origin of selected body raw materials, bonding materials, and special additives used to produce refractory products

Raw material	Typical composition	Applications	Source of supply
Body materials			
Silica	>95% SiO_2 silica rock	Production of fired silica brick for use in: coke ovens, glass tanks, roofs	Worldwide supplies of suitable material
	Silica sand	Production of sand molds for metal castings	
Chammotte	42–44% Al_2O_3 calcined aluminosilicate Low Fe_2O_3 (typically <1%) Low alkalis Low alkaline earths	Production of fired 42/44 Al_2O_3 aluminosilicate bricks for use in: blast furnaces; cement kilns; production of 42/44 aluminosilicate general purpose castable	Reserve of high-quality clay limited. Main supplies from South Africa, United States, China, and France
Andalusite	58–60% Al_2O_3 aluminosilicate mineral liberated from host rock Low Fe_2O_3 (typically <1.5%) Low alkalis Low alkaline earths	Production of fired 60% Al_2O_3 aluminosilicate bricks for use in: blast furnaces; steel ladles; torpedo ladles; and aluminum anode baking furnace	Reserve of high-quality andalusite limited. Main supplies from South Africa and France. China now entering the market
Bauxite	85–88% Al_2O_3 calcined aluminosilicate Fe_2O_3: <1.5%, TiO_2: <3.5% Low alkalis Low alkaline earths	Production of fired 85–88% Al_2O_3 aluminosilicate bricks for use in: steel ladles, torpedo ladles, and aluminum holding vessels Production of phosphate-bonded brick for aluminum remelt furnaces Production of castables	Reserves of high-quality ore limited to Guyana (gibbsite $Al_2O_3{\cdot}3H_2O$) and China (diaspore $Al_2O_3{\cdot}H_2O$)
Doloma	40% MgO, Fe_2O_3: <1.5%, SiO_2: <1%, Al_2O_3: <1%, CaO: ~56–60%	Production of fired doloma brick for use in: cement kiln hot zones; argon oxygen decarburization (AOD) vessels for stainless steel; and steel ladles	Reserves of dolomite for dead burning available in United States, Belgium, Germany, and United Kingdom
Magnesia	High-quality dead burnt magnesia Low porosity (bulk density >3.40 g/cm^3) Controlled CaO:SiO_2 ratio: >2.5:1) SiO_2: 0.5%, Fe_2O_3: <0.2%, Al_2O_3: <0.1%, B_2O_3: <0.05%, MgO: <96%	Used in the production of magnesia-carbon brick for basic oxygen steelmaking, electric arc furnaces, and steel ladles Used in the production of fired brick for glass tank regenerators, magnesia-spinel bricks for cement kilns, and slide gate plates High-quality magnesia chrome for use in secondary steel making	High-quality material sources from brine sea water and beneficiated natural magnesite found in Israel, Holland, Ireland, United Kingdom, United States, Greece, and Japan
	MgO: >90%	Used in the production of magnesia chrome, chrome-magnesia fired bricks for cement kilns, nonferrous (copper), and secondary steel making Also as a gumming repair material	Low-quality material sources from sea water and natural magnesite found in Greece, China, Brazil, and Czechoslovakia
Chrome ore	Iron chromite mineral: a mixed spinel of FeO, MgO, Fe_2O_3, Cr_2O_3, and Al_2O_3 Cr_2O_3 levels: 32–56%	Used in the production of fired magnesia-chrome and chrome-magnesia bricks	Supplied after separation from impurities from Phillipines, South Africa, and Zimbabwe
Graphite	Flake graphite mineral is separated from host rock Carbon level 85–95% Remainder aluminosilicate impurities	Used in the production of magnesia-carbon bricks and alumina-carbon, zirconia-carbon continuous casting products	Supplied from China, Norway, Sri Lanka, and Malagasy
Carbon	Electrocalcined or gas calcined anthracite or petroleum coke Carbon level >95% Remainder aluminosilicate impurities	Used in the production of fired carbon for blast furnaces and as the cathode in aluminum reduction cells	Supplied locally to suit market needs in United States, Germany, United Kingdom, and Poland
Alumina	Fused or tabular alumina: >99% Al_2O_3	Used in alumina carbon continuous casting products Fired alumina slide gates High-quality monolithics for the petrochemical industry and for blast furnace application	Produced by fusing or calcining Bayer grade alumina in United States, Holland, United Kingdom, and Japan
Aluminosilicate fiber	42–44% Al_2O_3 fiber produced from high-quality kaolinitic clay	Used as a fiber insulation in kilns, glass tanks, and so on	Produced in United States, Europe, and Japan
Mullite	Sintered or fused 72% Al_2O_3 aluminosilicate, $3Al_2O_3{\cdot}2SiO_2$	Creep-resistant refractory used as fired shapes in glass tanks, tunnel kilns, continuous casting	Produced in United States, United Kingdom, and Japan
Spinel	Sintered or fused magnesia aluminate, $MgO{\cdot}Al_2O_3$	Addition to fired magnesia bricks to improve thermal shock resistance for application in cement kilns and glass tanks	Produced in United States, United Kingdom, Germany, and Japan
Olivine	Naturally occurring magnesium silicate	Used as a monolithic coating in tundishes	Scandinavia
Silicon carbide	SiC produced by the Acheson process: >98% SiC Impurities: Si; SiO_2; C; and Fe_2O_3	Used as a nitride Sialon or self-bonded product in blast furnaces and aluminum reduction cells As a silicate-bonded product in incinerators and power plants	Norway and China
Zircon	Naturally occurring zirconium silicate sand, $ZrO_2{\cdot}SiO_2$, containing small quantities of HfO_2, Al_2O_3, TiO_2, and Fe_2O_3	Used in investment casting, foundries, as a glass contact refractory, an aluminum contact refractory Fluctuating demand as a ladle refractory Raw material for the production of zirconia and zirconia mullite	Australia, South Africa, and United States
Zirconia	Fused zirconia with ZrO_2 > 96% Main impurities: HfO_2; SiO_2 (<0.5%); Al_2O_3 (<0.5%); Fe_2O_3 (<0.1%); TiO_2 (0.2%)	Used in zirconia carbon continuous casting refractories as fired zirconia shapes, nozzles, kiln furniture, and so on, and as an addition to cement kiln doloma refractories to improve thermal shock resistance	Naturally occurring ZrO_2 (baddeleyite) found in South Africa Zirconia derived from zircon in United States, United Kingdom, and Germany
Zirconia mullite	Fused or sintered impurities in zircon diluted by high-purity mullite ($ZrO_2{\cdot}3Al_2O_3{\cdot}2SiO_2$)	Used in continuous casting refractories	United Kingdom, United States, and Japan

Table 3 Continued

Raw material	Typical composition	Applications	Source of supply
Bonding materials			
Lignosulfonates	...	Temporary green bond in fired refractories	By-product of the paper industry
Plastic clay	...	Permanent green bond in fired aluminosilicate refractories and for plastic bond in rammable monolithics	Widespread
Calcium aluminate cements	...	Permanent cementitious bond for castables	Japan, United States, France, and United Kingdom
Phosphoric acid	...	Permanent bond for low-temperature fired (400 °C, or 750 °F) refractories	Commodity chemical
Sodium silicate	...	Air setting bond for mortars	Commodity chemical
Tars/pitches	...	Bonding systems for carbon-containing products Materials carbonize on firing in reducing atmosphere Pitches also used to impregnate slide-gate refractories	By-product of coke plants and petrochemical refineries
Phenol formaldehyde resins, and furane resins	...	Bonding systems for magnesia graphite, alumina graphite, and zirconia graphite	Commodity chemicals
Special additives			
Volatilized silica	...	Used as an addition to low cement castables to improve rheological properties and sintering	By-product of the silicon industry Norway
Calcined alumina	...	Used as an addition to castables and high-quality alumina products to improve sintering	Produced from the Bayer process
Chromium oxide	...	Used as an addition to improve corrosion resistance in the presence of siliceous slags	Minor use of pigment grade Cr_2O_3
Silicon, aluminum	...	Used as powdered additives in carbon-bonded refractories to improve strength and improve oxidation resistance	Commodity materials
Proprietary phosphates	...	Used as dispersing aids in monolithic refractories	Commodity materials
Ethyl silicate	...	Used as a bond in special precast refractories	Commodity materials

kets are set to expand in real terms over the next few years.

Oxides. The main oxide materials in use today are alumina in spark plugs, substrates and wear applications; zirconia in oxygen sensors, as a component in lead-zirconium-titanate (PZT) piezoelectrics, wear applications, and thermal barrier coatings; titanates in barium titanate capacitors and PZT piezoelectrics; and ferrites in permanent magnets, magnetic recording heads, memory devices, temperature sensors, and electric motor parts.

Carbides and Nitrides. Carbides (mainly silicon carbide and boron carbide) are used in wear applications while nitrides (mainly silicon nitride and Sialon) are used in wear applications and cutting tools. Aluminum nitride with its high thermal conductivity is the primary contending material for part of the electronics substrate market currently dominated by alumina. In addition, aluminum nitride is a key component in the production of Sialons from silicon nitride:

$$Si_3N_4 + AlN + Al_2O_3 \rightarrow Si_3Al_3O_3N_5 \quad \text{(Eq 1)}$$

Mixed Oxide Ceramics. Ceramics research and development efforts are focused on a number of new applications for ceramics that all have enormous potential. Three significant applications are:

- Ceramic superconductors
- Ceramics for solid oxide fuel cells
- Ceramic components for heat engines

Ceramic superconductors are based on a number of mixed oxide systems that include $YBa_2Cu_3O_{7-\delta}$, $Bi_2Sr_2CaCu_2O_8$, and $Bi_2Sr_2Ca_2Cu_3O_{10}$ stabilized with PbO. Solid oxide fuel-cell ceramics are based on ionic conductors in which high-purity stabilized zirconia is currently the material of choice. Ceramic heat-engine components under investigation are composed of silicon carbide, Sialons, and zirconia either as single-phase ceramics, ceramic-ceramic composites, or metal-matrix composites (MMCs).

Processing Innovations. Research and development activity is generating new technologies for the production of ceramic materials. Precursor derived ceramics are estimated to have a market value of $200,000,000 in 1989, the major part of which is in chemical vapor deposition (CVD) (86% of the total market value). Other segments of this growing market include chemical vapor infiltration (CVI), sol-gel, and polymer pyrolysis. Products that are being successfully produced by these means include continuous ceramic fibers, composites, membranes, and ultra-high-purity/high-activity powders.

Table 4 Estimated market for advanced ceramic powders in the United States from 1989 to 1995 categorized by applications and types of material

	1989		1990		1995		
Product	Percent	Monetary value, 10^6 dollars	Percent	Monetary value, 10^6 dollars	Percent	Monetary value, 10^6 dollars	1989–1995 growth rate, %/yr
Application							
Electronic	81.6	340.5	81.2	374.1	80.8	561.0	8.5
Structures	13.3	55.6	14.0	64.2	15.3	105.9	10.5
Coating	5.1	21.3	4.8	22.2	3.9	27.0	4.0
Total	**100.0**	**417.4**	**100.0**	**460.5**	**100.0**	**693.9**	**8.5**
Material type							
Oxides	88.2	368.0	87.7	404.0	87.8	608.9	8.5
Carbides	9.8	41.0	10.0	46.0	9.4	65.0	7.1
Nitrides	2.0	8.4	2.3	10.5	2.8	20.0	13.8
Total	**100.0**	**417.4**	**100.0**	**460.5**	**100.0**	**693.9**	**8.5**

Table 5 Raw materials for advanced structural and magnetic (ferrite) ceramics

End product	Raw materials	Key product properties	Applications
Al_2O_3	Bayer process alumina derived from bauxite	Low permittivity Hardness Wear resistance	Substrates, insulators, spark plugs, wear parts, milling media, thread guides, armor, radomes
ZrO_2	Zirconia derived from zircon by chemical processes	Ionic conductivity Electronic conductivity Wear resistance	Oxygen sensors, fuel cells (potential), high-temperature heater, milling media
CBN	High temperature and pressure transformation of hexagonal form of BN (HBN) (formed by reacting B_2O_3 and urea in nitrogen)	High thermal conductivity High electrical resistivity High hardness	Substrates in electronics Machining of ferrous metals
BeO	Beryllia powder from beryl or bertrandite ores	High thermal conductivity High electrical resistivity	Substrates (heatsinks) in electronics
SiC	Acheson process: $SiO_2 + C \rightarrow SiC + CO$ Pyrolysis of polycarbosilanes	Extreme hardness Resistance to thermal shock	Wear parts As a fiber whisker or particle in MMCs and CMCs
$Al_2O_3{\cdot}ZrO_2$	High-quality alumina High-quality zirconia	Improvement in strength and toughness over Al_2O_3	Wear parts
Si_3N_4	Silicon nitride powder derived from silicon and nitrogen	Hardness Resistance to thermal shock	Wear parts
Sialons	Silicon nitride, alumina, 21R polytype (AlN), yttria	Hardness Toughness Resistance to thermal shock	Wear parts Extrusion dies Cutting tools
AlN	AlN powder, prepared by carbothermal reduction of Al_2O_3 in nitrogen, or direct nitridation of Al	Low permittivity High thermal conductivity	Electronic substrates
SnO_2	High-purity tin dissolved in nitric acid and coprecipitated with other oxides	Surface controlled conductivity	Sensors
PZT (lead zirconium titanate)	High-purity oxides Coprecipitated oxides	High piezoelectric coefficients Change of polarization with temperature	Transducers Actuators Pyroelectrics
PMN (lead magnesium niobate)	High-purity oxides Coprecipitated oxides	High permittivity and breakdown voltage Controlled deformation in an applied field	Capacitors Actuators
PLZT (lead lanthanum zirconium titanate)	High-purity oxides Coprecipitated oxides Metal alkoxide-based coatings	Change of birefringence with applied field Controlled deformation in an applied field Change of birefringence with applied field	Electro-optics, head-up displays, flash goggles Actuators
ZTS (zirconium titanium stannate)	High-purity oxides	Stable permittivity at high frequencies over a wide temperature range and very low dielectric and insertion losses	Microwave resonators and filters
PBNT ($PbO{\cdot}BaO{\cdot}Nd_2O_3{\cdot}TiO_2$)	High-purity oxides	Stable permittivity at high frequencies over a wide temperature range and very low dielectric and insertion losses	Microwave resonators and filters
ZnO	High-purity oxides (derived from metal smelting) plus praeseodymium or bismuth oxides	Change of resistivity with applied field	Varistors
$YBa_2Cu_3O_{7-\delta}$	Barium, strontium, calcium salts (chlorides, carbonates, nitrates, and peroxides)	Superconductivity	Demonstration devices
$Bi_2Sr_2CaCu_2O_8$	Barium, strontium, calcium salts (chlorides, carbonates, nitrates, and peroxides)	Superconductivity Very low insertion losses	Microwave filters
$Bi_2Sr_2Ca_2Cu_3O_{10}$ stabilized with PbO	High-purity oxides Coprecipitation, sol-gel, metal alkoxides, sputtering, chemical vapor deposition	Superconductivity conductor in very high magnetic fields	Nuclear magnetic resonance (NMR) imagers
TiB_2	Powder made by carbothermal reduction of TiO_2 with B_2O_3	Electrical conductivity Resistance to molten aluminum coupled with complete wetting of surface	Potential cathode material in primary aluminum production Evaporator boats (with BN)
B_4C	Carbothermal of reduction B_2O_3	Very hard Abrasion resistant Absorbs thermal neutrons	Shot blast nozzles, bearings, armor, and nuclear energy industry uses
Ferrites			
Hard ferrites			
$SrFe_{12}O_{19}$	$SrCO_3/Fe_2O_3$	High residual flux density High coercive force	Permanent magnets
$BaFe_{12}O_{19}$	$BaCO_3/Fe_2O_3$	High coercive force High residual flux	Motors
Soft ferrites			
$MnZnFe_4O_8$	Mixed oxide, iron oxide derived from thermal hydrolysis of ferric chloride	High initial permeability Low loss	Wide band/pulse, transformers Inductors, telecommunications
$MnNiFe_4O_8$	Mixed oxide, iron oxide derived from thermal hydrolysis of ferric chloride	High initial permeability High saturation flux density	Wide band/pulse, transformers Power transformers, magnetic recording heads
Microwave			
$Y_3Fe_5O_{12}$	Coprecipitation or milling of pure oxides	Narrow line widths and extremely low losses at microwave frequencies	Elements in microwave circuitry
$BaTiO_3$	Barium carbonate and titania Barium chloride and titanium tetrachloride	High permittivity High breakdown voltage Increase of resistance with increase of temperature High piezoelectric coefficients Change of birefringence with field	Capacitors Positive temperature coefficient (PTC) thermistors Transducers, actuators Electro-optics

The main products of the advanced ceramics industry, both existing and potential, are listed in Table 5, which indicates the key end property requirements, the main applications, and the raw material base for the products. The processes used to convert these raw materials to finished products include additional powder processing (for example, milling and spray drying) prior to forming green shapes that are then fired under controlled conditions. The forming processes include die pressing, isostatic pressing, slip casting, tape casting, extrusion, injection molding, hot pressing, hot isostatic pressing (HIP), chemical vapor deposition (CVD), and so on.

Chemical Additives to Aid Ceramic Processing. Each step in the manufacturing process requires careful control so that end product properties are obtained at maximum production efficiency and key effect chemicals are used to optimize powder treatment and green forming. The effect chemicals include milling aids, flocculants and binders, lubricants to effect product release during pressing and minimize wear of die parts, and plasticizers to aid extrusion and injection molding. A list of such chemicals is shown in Table 6. While these materials play an important economic role in production, they are burnt out during firing and play no part in the final product chemistry. The burn out process has to be carefully controlled to avoid residual carbon in the finished products and process research and development is continuously investigating ways of minimizing the levels of effect chemicals used.

In addition to spawning ceramic products and ceramic manufacturing technologies for new applications, the influence of the advanced ceramics industry on the traditional ceramics industry should not be overlooked. It is judged that many high-technology materials and processes will find application in the traditional ceramics industry as the latter strives to reduce manufacturing costs, to improve quali… and to give better value in service to the … user.

Primar… Ceramic Raw Materi…s

From the … ta presented under the application secti… in Tables 3 and 5 it is apparent that the … re certain key materials that are either u… directly by the ceramics industry or th… epresent the starting point for the producti… of added value materials:

- Silica
- Clay
- Alumina
- Magnesi…
- Titania
- Iron oxi…
- Zircon/z…nia

This discu…n will focus on the properties of silica, alu…a, and zircon/zirconia.

Silica

Silica, in … ition to its use in refractories and whitewa…, is also the starting point in the manufact… of elemental silicon, silicon carbide, and … con tetrachloride. Silicon, in turn, is the s… ing point for silicon nitride, and silicon t… chloride is the precursor for a wide range … silicon organics that can be pyrolyzed un… controlled conditions to high-quality silic… carbide and silicon nitride. Thus, there … choice, albeit at a price to obtain silico… itride and silicon carbide at different stat… of purity and activity. Currently, silico… rbide (prepared by the Acheson process i… hich a mix of silica and coke is heated ele… cally to 2400 °C, or 4350 °F) is used as a … actory in blast furnaces, incinerators, p… r stations, aluminum reduction cells, a… copper refining while high-purity powde… lso prepared by the Acheson process) can b… sed to make engineering wear parts such as … ls, pump parts, bearings, and dies. The pow… r is also used in metal-matrix composites. … con carbide has been derived from polycarbosilanes by pyrolysis in both powder and fiber form and, despite its high price, represents a potential for producing ceramic/ceramic composites.

Silicon nitride and its Sialon derivatives and silicon carbide despite their tendency to oxidize, have the potential to meet many of the property targets set by the heat engine market. A feature of silica and the ceramic materials that are derived from silica is that all the elements are readily available in the earth's crust. In this respect, these materials offer the potential of ease of supply in all parts of the world. In practice, however, there is a significant energy input required to produce silicon and silicon carbide. Consequently, manufacture of these materials is by and large limited to countries with cheap and readily available electric power (for example, Scandinavia and North America).

A flowchart relating silica to materials used (or with prospects of use) in the ceramics industry is shown in Fig 1.

Table 6 Selected chemical additives used to opt…ize powder treatment and green forming of ceramics

Material	…plication or function
Polyvinyl alcohol	Binder for advanc… eramics
Polyethylene glycol	Binder for advanc… eramics
Sodium polyacrylate	Deflocculant for s… asting
Tertiary amide polymer	Binder for dry pre… g
Starch blended with dry colloidal aluminosilicate	Binder for vacuum … ming
Cationic alumina plus organic flocculant	Binder for vacuum … ming
Pregelled, cationic corn starch	Flocculant for coll… l silica and alumina binder
High-purity sodium carboxymethylcellulose	Binder
Inorganic colloidal magnesium aluminum silicate	Suspending agent
Medium-viscosity sodium carboxymethylcellulose added to Veegum	Suspending agent, … cosity stabilizer
Ammonium polyelectrolyte	Dispersing agent f… asting slips for electronic ceramics
Sodium polyelectrolyte	Dispersing agent b… r for spray-dried bodies
Microcrystalline cellulose and sodium carboxymethylcellulose	Thickening agent
Polysilazane	Processing aid, bi…, and precursor for advanced ceramics

Source: Ref 30

Alumina

Alumina is found throughout the earth's crust as a component in aluminosilicate minerals. Economics dictates that alumina be extracted from bauxite using the Bayer process. Bauxite is widespread in the equatorial belt in different states of purity and is divided into two classifications: refractory grade ore and metallurgical ore.

Refractory grade bauxite is supplied by China and Guyana as a high-temperature calcine of the naturally occurring mineral: diaspore ($Al_2O_3 \cdot H_2O$) in China and gibbsite ($Al_2O_3 \cdot 3H_2O$) in Guyana. Both calcines conform to controlled chemical and physical specifications (for example, alumina 80 to 88%, and minimal levels of fluxing impurities) and are used in a wide range of refractory brick and monolithic compositions. During calcination, a complex phase assemblence of corundum (Al_2O_3), mullite, a silica glass, and minor levels of aluminum titanate is formed. The consumption of refractory grade bauxite exceeds 700,000 tonnes/yr (800,000 tons/yr) on a worldwide basis.

Metallurgical grade bauxite is mined in Australia, Jamaica, and West Africa and

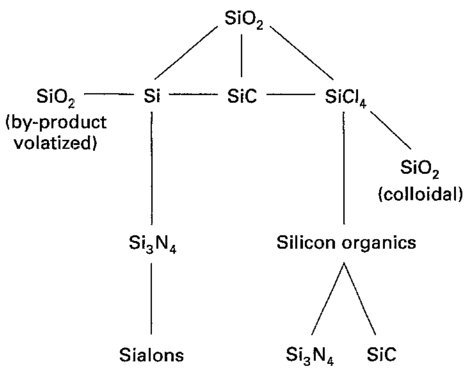

Fig 1 Use of silica as a precursor for ceramics

has a variable alumina level in conjunction with major impurities such as iron oxide and silica. The alumina in the metallurgical ores is extracted from the ore when dissolved by sodium hydroxide, yielding a sodium aluminate solution that is separated from the iron oxide and silica, which are rejected as a waste product in the form of red mud. Essentially, pure aluminum hydroxide is precipitated from the sodium aluminate and then calcined to a number of grades of alumina. In 1989, the world production of alumina was approximately 39 × 10^6 tonnes (43 × 10^6 tons), which compares to 37.5 × 10^6 tonnes (41.3 × 10^6 tons) in 1988 and 35 × 10^6 tonnes (39 × 10^6 tons) in 1987. Approximately 92% of alumina produced by this method is used to produce aluminum by the Hall-Heroult process, with the remainder finding a diverse range of chemical and ceramic applications. Current reserves of metallurgical grade bauxite are more than adequate to meet the demand predicted for the next 200 years.

The high-purity aluminas used in the ceramics industry and derived by the Bayer process are classified as:

- Tabular alumina
- Fused alumina
- Specialty calcined alumina

Tabular alumina is produced by high-temperature (~2000 °C, or 3630 °F) calcination of low-temperature calcined alumina in large oil-fired rotary kilns. Fused alumina is produced by the electric melting of calcined alumina. Both materials contain >99.5% Al_2O_3 with Na_2O as the major impurity at ≤0.3% and have a grain porosity of <5%. Tabular and fused alumina are sold to the refractory industry in crushed and graded form for use in a wide range of high-quality products:

- Continuous casting refractories (for example, single-edge notched or SEN/slide gates)
- Monolithic refractories for application in blast furnaces and the petrochemical industry

Specialty calcined alumina powders are the major raw materials used in the advanced ceramics industry for both electronic and engineering applications. The powders are produced in a wide range of grades against exacting specifications of chemistry, particle size, and crystal type to suit a wide range of end product applications. The normal 0.5% Na_2O level of Bayer process alumina can be reduced to make specialty low soda grades during refining/calcination while physical properties can be adjusted during rotary kiln calcination and subsequent dry grinding. Current trends lean toward improved grinding control to produce materials with median particle sizes up to 0.5 μm (20 μin.) as well as in the supply of spray dried granules that can be fed directly into customer's plant.

There is an established international trade in high-quality aluminas but, with many of the ceramic manufacturers having in-house milling and spray drying facilities, there is clearly a limitation to the growth in the supply of spray dried systems and a continuing need to supply aluminas which match the customer plants so that use of the latter can be optimized at an acceptable price.

Alumina is a significant ceramic material that is available at a high degree of purity. The dominant position of alumina as a ceramic raw material arises because it has desirable properties at a relatively low cost. This cost-effectiveness is attributable to the commodity nature of the business arising from the large demand for alumina by the aluminum industry.

Zircon and Zirconia (Ref 31–34)

The primary source of zirconia is the mineral zircon ($ZrO_2 \cdot SiO_2$), which exists in beach sands principally in Australia, South Africa, and the United States. The production of zircon from 1984 to 1988 is shown in Table 7. In addition, the mineral baddeleyite (ZrO_2) is sourced as a by-product of a phosphate deposit in South Africa.

Zircon extracted from beach sands contains ~2% HfO_2 and traces of Al_2O_3 (<0.5%), Fe_2O_3 (<0.1%) and TiO_2 (<0.1%). In addition, all zircons contain traces of uranium and thorium. The radioactivity inherent in zircon and in zirconia prepared from zircon is generally well within existing hazardous material legislation limits and careful control and monitoring is undertaken to ensure compliance. Baddeleyite also contains similar trace impurities but significantly higher radioactivity and often higher than the 500 ppm limit. The exceeding of the specification limit is making the material increasingly difficult to market in countries such as the United States where legislation is being tightened and regulations strictly enforced.

Zircon is processed by fine grinding to produce a range of milled products of defined particle size. These products have found use in investment casting, foundries, refractory products, and as an opacifier in glazes for whitewares.

Zircon is also the principal source of zirconia. Zircon can be chlorinated in the presence of carbon to give zirconium and silicon tetrachlorides that are then separated by distillation. The zirconium tetrachloride produced can be used to prepare zirconia directly or as a feedstock for other zirconium chemicals. Sintering with alkali or alkaline earth oxides is also used to decompose zircon. Silica is leached from the decomposition products with water, leaving zirconium hydroxide to be further purified by acid dissolution and reprecipitation. Zirconia is then obtained by calcining the hydroxide. Zircon is also converted to zirconia and silica in a plasma at >1800 °C (>3270 °F) with rapid cooling to prevent reassociation. The free silica is removed by dissolution in sodium hydroxide. Fused zirconia is produced in electric arc furnaces from either baddeleyite or zircon/carbon feedstocks. In the latter process, the silica component of zircon is carbothermally reduced to silicon monoxide, which volatilizes prior to the fusion of the residual zirconia.

Zirconia is normally sold as a stabilized or partially stabilized product for use in high-temperature applications so that the effect of the phase transition at ~1100 °C (~2010 °F) from monolithic to cubic/tetragonal is negated. Stabilization is effected by additives containing Ca^{2+}, Mg^{2+}, Y^{3+}, or Ce^{4+} at the

Table 7 World zircon production from 1984 to 1988

	Amount produced annually									
	1984		1985		1986		1987		1988	
Country	tonne × 10^3	ton × 10^3	tonne × 10^3	ton × 10^3	tonne × 10^3	ton × 10^3	tonne × 10^3	ton × 10^3	tonne × 10^3	ton × 10^3
Australia	458	504	501	551	452	497	457	503	490	540
South Africa	153	168	161	177	140	154	140	154	150	165
United States	113(a)	124(a)	113(a)	124(a)	113(a)	124(a)	113(a)	124(a)	118(b)	130(b)
USSR	80	90	85	94	85	94	85	94	85	94
Brazil	6	7	21	23	15	17	18	20	20	22
Malaysia	8	9	12	13	13	14	18	20	19	21
India	12	13	15	17	16	18	16	18	17	19
China	15	17	15	17	15	17	15	17	15	17
Other countries	4	4.4	5	5.5	6	7	5	5.5	9	10
Total	**849**	**934**	**928**	**1020**	**855**	**940**	**867**	**955.5**	**923**	**1015**

(a) U.S. production capacity estimated by USBM. (U.S. Bureau of Mines). (b) Actual reported to USBM. Source: USBM. Minerals Yearbook, 1988.
Source: Ref 33

precipitation stage or as oxides in the fusion process.

The purity of the zirconias produced varies from process to process. All contain HfO_2, typical fused products contain 0.2 to 0.5% SiO_2, 0.1% Al_2O_3, 0.05 to 0.1% Fe_2O_3, and TiO_2, while high-quality materials via precipitation/plasma routes can be produced with silicon dioxide, aluminum oxide, ferric oxide, and titanium dioxide impurities at the ppm level. The end uses for zirconia include refractories, ceramic colors, thermal barrier coatings, oxygen sensors, additions to lead zirconium titanates, and gemstones. Each application demands different specifications and costs range from \$5 to \$200/kg (\$2.30 to \$90/lb). Existing applications all represent growth areas and the potential use of zirconia in solid oxide fuel cells could markedly increase future demand.

Future Outlook

The traditional markets of building products, whitewares, and refractories represent significant businesses with low growth but new industries such as electronics are rapidly becoming as economically important. Significant research and development expenditures are defining new potential for ceramics in terms of materials, methods of production, and applications. It is projected that there will be future growth in ceramics for metal-matrix composites, ceramic-matrix composites, and in advanced processing such as sol-gel, chemical vapor deposition, and polymer pyrolysis.

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