37

Industry and the Environment

CHAPTER PREVIEW

Throughout this book we have highlighted the engineering applications for ceramics. In the final analysis the importance of any material is based on the applications for which it can be used. For example, at the present time high-temperature superconductors (HTSC) are of research interest but are not commercially so important. Because of the unparalleled range of properties shown by ceramics they find application in a vast number of areas. This last chapter looks at the field from an industrial perspective. Because it is impossible to cover every aspect of the multibillion-dollar ceramic industry in one chapter we have chosen to focus on a few topics, mainly through examining case studies. One of the exciting prospects for the industry over the next decade is in nanotechnology. Ceramic nanopowders already represent the largest segment of the nanopowders market and are used for polishing and sunscreens, etc. With the demonstration of the successful growth of ceramic nanowires, nanosprings, and nanotubes, the potential exists for even more applications in critical areas such as hydrogen storage. As we have often done we begin with some history.

37.1 THE BEGINNING OF THE MODERN CERAMICS INDUSTRY

In Chapter 2 we described some of the early history of ceramics and their production. The transition to a large-scale manufacturing industry occurred in Western Europe during the eighteenth century as part of the period that became known as the Industrial Revolution. The great porcelain factories established, and subsidized, by royal patronage at Mießen in Germany and Sèvres in France began to give way to purely commercial products being made in Staffordshire in the north of England. Later the factories at Mießen and Sèvres began to imitate English designs. They were certainly helped in this area by immigrant workers. Emigration was a concern for the ceramics industry more than many others, such as iron production, because it relied on secret processes, such as specific body and glaze compositions. Once these became known a worker would become valuable to a competitor.

The development of the Staffordshire area as the prominent pottery center in England was in large part due to the use of coal as a fuel for the kilns. Coal was abundant in this area as

> **SÈVRES**
>
> *Royal Commission*: The factory at Sèvres was commissioned to make an 800-piece dinner service for Catherine II of Russia. It took 3 years to complete.

> **SIX TOWNS: THE POTTERIES**
> Tunstall, Burslem, Hanley, Stoke-upon-Trent, Fenton, and Longton

was, and still is, a source of clay. The proximity of raw materials provided an economic advantage over other rural potteries that were still using a diminishing supply of timber. Staffordshire is a long way from the major metropolitan areas of London, Bristol, and Norwich. Early pictures of Tunstall, one of the six towns that formed the Potteries and in 1910 became absorbed into the city of Stoke-on-Trent, show a town surrounded by hilly countryside. By the mid-eighteenth century there were many separate potteries employing a large number of workers. A petition presented before the British Parliament in 1763 read:

In Burslem [another of the six towns that made up the Potteries] and its neighborhoods (*sic*) are nearly 150 separate potteries for making various kinds of stone and earthenware, which, together, find constant employment and support for nearly 7,000 people.

In the early days of the pottery industry in England, transport of raw materials in and product out was inefficient. The costs of transportation had to be included in the selling price of every article produced. Clearly, quantity production could not be achieved without better transportation.

Master potter and entrepreneur Josiah Wedgwood was instrumental in organizing a potters' association to push for the development of improved roads and a canal system. Wedgwood realized that cheaper and more regular transport meant an even flow of production, fewer breakages, lower prices, wider markets, and greater sales. Staffordshire potters lobbied successfully for the development of a canal that would link the rivers Trent and Mersey, which was authorized by an Act of Parliament in May 1766. The project was completed in 1772 at a total cost of £300,000. The completion of the Trent-Mersey Canal ensured that Staffordshire would remain the center of English pottery production. A complex web of railway routes followed and these developments transformed an isolated rural area into a major industrial center.

Wedgwood made contributions in several areas that helped transform the production of pottery into a major industry. He changed the manufacturing process and adopted mechanization that would enable him to increase production while lowering prices; the increased productivity helped to maintain a stable wage for his employees. He had many ideas about sales and marketing of his products and was the first manufacturer to introduce the "satisfaction-guaranteed-or-your-money-back" policy, which is now an extensively used tool for selling.

Wedgwood was an advocate of free trade and a commercial treaty with France was welcomed by many of the ceramic manufacturers as a means of stimulating imports. Industries that had not adapted to new technology, such as the use of steam, feared the competition of imports. Wedgwood wrote on this issue of the treaty with France:

An exchange of the produce of one nation for the manufactures of another are happy circumstances, and bid fair to make the intercourse lasting; but sensible as I am to the interests of trade, manufacturers and commerce, they all give place to a consideration much superior in my mind to them all. I mean the probability that a friendly intercourse with so near and valuable a neighbour (*sic*), may keep us in peace with her—may help to do away with prejudices as foolish as they are deeply rooted, and may totally eradicate that most sottish and wicked idea of our being natural enemies . . . .

The production of ceramics became an important and growing export industry. Vast quantities of ceramic ware produced in the Potteries were exported from the major seaports of London, Bristol, Liverpool, and Hull to America, the West Indies, and all over Europe.

Today many of the most famous names associated with the Staffordshire Potteries are still thriving companies, such as Royal Doulton and Spode. A visit to any department store will demonstrate that these companies are still regarded as producing some of the highest quality ceramic

tableware. Wedgwood merged in 1986 with Waterford Crystal forming Waterford Wedgwood plc to become the world's largest tableware company with sales in excess of $1 billion. As with other industries the ceramic industry has seen much consolidation and acquisition in recent years.

37.2 GROWTH AND GLOBALIZATION

Although the UK was a traditional leader in the development of ceramics, there were major changes during the latter half of the twentieth century when Japan became the major producer of ceramics. Rapid transportation routes meant that manufacturing sites no longer needed to be near mineral resources. For example, Japan has no significant domestic energy supplies but is a major industrialized manufacturing nation. One of the significant changes that led to the growth and dominance of Japan was a shift in its business from traditional low value-added basic ceramics to one that has a large component of high value added. Table 37.1 shows the market for high technology ceramics as it was in 1980. Japanese companies satisfied about half of the $4.25 billion demand. In some areas they were dominant, producing over 60% of the worldwide market for integrated circuit (IC) packages and almost 80% of the ferrites. The market for IC packages, which is based on alumina, was established largely by U.S. companies, but there are few remaining that sell on the open market.

The rapid growth in the Japanese production of ferrites in the 1970s and 1980s coincided with a decline in this area in the United States and in Europe. The only serious constraint on the expanded production of ferrites in Japan during this period was a shortage of raw material (secondary iron oxide) caused by weak steel production.

CERAMIC IC PACKAGES

Together with substrates, ceramic packages compete with polymers but are superior in terms of thermal conductivity and hermeticity and are used in high-reliability applications.

TABLE 37.1 The 1980 Market for High Technology Ceramics[a]

Product	Japan	World
Ceramic powders	$130	$250
Electronic IC packages/substrates	540	880
Capacitors	325	750
Piezoelectrics	295	325
Thermistor/varistors	125	200
Ferrites	380	480
Gas/humidity sensors	5	45
Translucent ceramics	20	45
Cutting tools: carbide, cermet, coated noncarbide	120	1000
Structural ceramics (heat and wear resistant)	120	250
Totals	$2065	$4250

[a] In millions of dollars; excluding fibers, nuclear fuels, and spark plugs.

TABLE 37.2 Challenges Facing the Ceramic Industry According to Percentage of Survey Respondents

Environmental standards	39%
Changing markets	33%
Cost of labor	32%
Imports	27%
Health and safety standards	26%
Cost of materials	25%
Quality of labor	20%
Capital for expansion	20%
Quality control	19%
Cost of fuel	19%

Table 37.2 shows some of the challenges that face ceramics companies worldwide. This information was gathered from a survey of over 250 ceramics companies. The major challenges are meeting environmental standards, adapting to changing markets, and labor costs.

The ceramics industry, like many others, can establish production facilities in which labor costs are lower. For example, KEMET Corporation based in Greenville, SC, a manufacturer of tantalum electrolytic and multilayer ceramic chip capacitors, is relocating all manufacturing to lower-cost facilities in Mexico and China.

37.3 TYPES OF MARKET

As we described in Chapter 1, the ceramics industry is generally divided into six distinct markets:

- Glass
- Advanced ceramics
- Whiteware
- Porcelain enamel
- Refractories
- Structural clay

It is in advanced ceramics that many of the exciting developments are occurring. The average annual growth rate of the U. S. advanced ceramics market during the past 5 years was about 8% (now currently $12 billion). The largest growth segments are electronic ceramics, which includes capacitors, piezoelectrics, and ferrites. In chemical processing and environmental-related applications ceramics are used for automotive catalyst supports and filters that are being increasingly employed to reduce pollutants in response to regulations on both automobile and industrial emissions.

37.4 CASE STUDIES

Again following Chapter 1, the ceramics industry covers a wide range of materials and products. We can generally divide the activities of this industry into three distinct categories as listed, with examples, in Table 37.3. In this section we describe in more detail one example of each activity and some current industrial trends.

Silicon Nitride Powder

Silicon nitride, Si_3N_4, is not a naturally occurring mineral. All the Si_3N_4 that we use must be synthesized, usually by one of the following methods (more details are given in Chapter 19):

- Direct nitridation of Si
- Carbothermal reduction of silica in N_2
- Vapor phase reaction of $SiCl_4$ or silane (SiH_4) with ammonia

The following characteristics of the resulting powder are important to end-users:

- *Particle size and distribution*. Powder compacts containing a few coarse particles produce components with significantly reduced strength and toughness (two of the properties we are often trying to maximize). Milling can be used to reduce particle size but often leads to significantly increased costs and the introduction of unwanted contamination.
- *Surface area*. This affects how easily the powder can be densified during sintering and the final grain size in the sintered component.
- *Purity*. Purity depends on the processing route and wide variations are possible. Oxygen on the surface of the powders can affect densification, however, we need enough to form the liquid phase during sintering.
- *Structure*. A high α-Si_3N_4 content is desirable because this favors the conversion to rodlike interlocking β-Si_3N_4 during subsequent processing into bulk components as illustrated in Figure 37.1.

The cost of Si_3N_4 powders can vary from $30/kg up to $150/kg depending on particle size and purity. The high costs of raw material and the subsequent shaping and

TABLE 37.3 Types of Ceramic Industry

| Activity	Examples
Ceramic powders	SiC for abrasives
	Nanosized TiO_2 for sunscreen
	Bioactive glasses for bone reconstruction
	Bayer process Al_2O_3 for the production of Al using Hall–Héroult cells
Forming powders into bulk forms	Slip casting of toilet bowls
	CZ growth of Nd:YAG single crystals
	AlN sheets by tape casting
	Glass melting
Fabricating ceramic components	Ceramic chip capacitors
	Packages for integrated circuits
	SiC pressure sensors
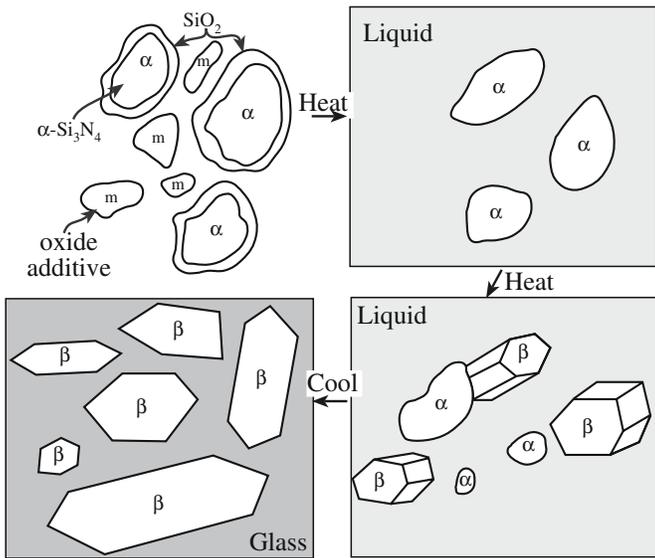
FIGURE 37.1 Schematic showing processing steps in forming Si_3N_4 by liquid phase sintering (LPS). The metal oxide additive (m) would be something like Y_2O_3 and the liquid an oxynitride/silicate.

TABLE 37.4 Summary of Costs for Direct-Nitrided Si_3N_4 Powder

Cost distribution	$/kg	% of total
By cost element		
Silicon powder	7.49	25.4
Silicon nitride seed powder	1.71	5.8
Capital equipment	0.49	1.7
Direct labor	1.18	4.0
Energy	1.88	6.4
Process materials	16.74	56.8
Total	29.48	100.0
By process step		
Silicon powder	7.49	25.4
Silicon nitride seed powder	1.71	5.8
Direct nitriding	3.30	11.2
Crushing	6.62	29.3
Fine grinding	8.36	28.4
Total	29.48	100.0

forming processes have restricted the use of Si_3N_4. Table 37.4 shows a summary of a cost analysis performed for direct-nitrided Si_3N_4 powder. Most of the cost of the powder is due to the raw materials and the process materials—namely the milling media. Si_3N_4 milling media is very expensive; it costs about $150/kg, as compared with alumina or steel media at $16/kg and $4/kg, respectively.

Some of the present applications for Si_3N_4 parts

EIA CAPACITOR CODE

The size of MLCCs is "llww": ll is the length of the capacitor and ww is the width, both in thousandths of an inch (a case where Imperial and U.S. units are still widely used in industry!) *Example*: 0805 means a capacitor of length 0.080 in. (~2 mm) and width 0.050 in. (~1.25 mm).

include cutting tool inserts, bearings and rollers, refractory parts, cam followers in engines blades, vanes in heat engines, and turbocharger rotors. The advantage of using Si_3N_4 for cutting tool inserts should be clear from Figure 37.2. The units are given as SFM, surface feet per minute, which is a measure of the distance covered by a rotating tool (traditionally a saw or lathe now used in wear); the surface foot is a linear foot (3.28 SF = 1 m).

There are several powder manufacturers, primarily in Germany and Japan, producing hundreds of tons of Si_3N_4. There are currently no U.S. suppliers of Si_3N_4 powder. GTE, Dow Chemical, and Ford Motor Company developed high-quality Si_3N_4 powders between about 1973 and 1995, but none of these companies is a supplier today.

Ceramic Chip Capacitors

We described the structure of a multiplayer chip capacitor (MLCC) in Chapter 31. They are used in a large number of products, in particular, personal computers and cell phones. A typical cell phone may contain 400 MLCCs. The goal is to make smaller components with larger capacitances at a lower cost.

Capacitors are extremely price competitive because of their relatively simple structure (see Figure 31.18). The following costs are involved:

- The ceramic dielectric. The ceramic capacitor industry uses more than 10,000 tons of $BaTiO_3$-based dielectrics (about 90% of the total produced).
- The metal electrodes are usually precious metal based.
- Labor costs are particularly important in this industry because of the low value-added costs.

Figure 37.3 shows the trend in the size of MLCCs since 1981. The designations used follow the Electronic Industries Association (EIA) guidelines. In the 1980s most MLCCs produced were either 1206 or 0805 (the two largest sizes). By 2000, the 1206 accounted for less than 10% of the market, while 30% of the market was for the 0402: a component with a fraction of the area and using much less material. Since 2000, the very small 0201 has captured an increasingly larger market share.

The use of lower operating voltages in handheld devices and microprocessors has allowed dielectric layer thickness to be reduced; consequently higher layer counts are possible within the same overall device dimensions, as shown in Figure 37.4.

You may recall from Chapter 31 that capacitance, C, is given by
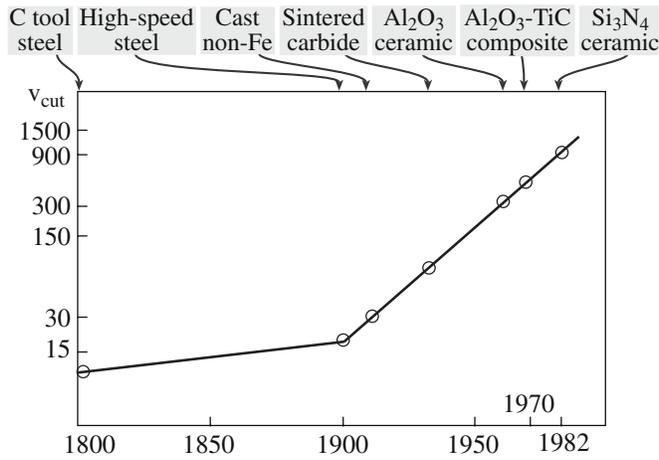
$$C = \kappa\varepsilon_0 A/d \qquad (31.13)$$

FIGURE 37.2 Improvements in the rate of metal cutting for various cutting-tool inserts.

FIGURE 37.4 Trends in number (N) of dielectric layers and thickness (Δ) of the dielectric layer.

By reducing d and increasing the number of layers (effectively increasing A) it has been possible to expand the capacitance of MLCCs into the tantalum and aluminum electrolytic capacitor range.

The ability to cast thin layers ($\times 3\,\mu m$) requires highly disperse, uniform, fine-grained ceramic powders (100–300 nm particle diameter). To achieve these particles sizes extensive milling may be used or the powder can be made by solution methods such as using metal alkoxides as described in Chapter 22.

A major challenge in the MLCC industry has been to replace the precious metal electrodes (usually a Pd–Ag alloy) with base metals such as Ni. The MLCC industry accounts for about 75% of the electronic industries use of palladium.

Nd-Doped YAG Laser Crystals

Yttrium aluminum garnet (YAG) single crystals are the most widely used laser host, with over 100,000 YAG lasers
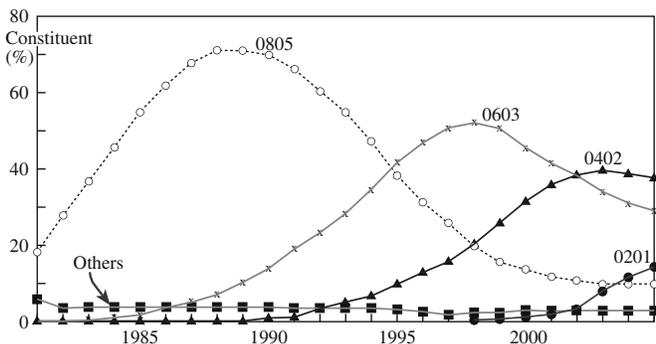

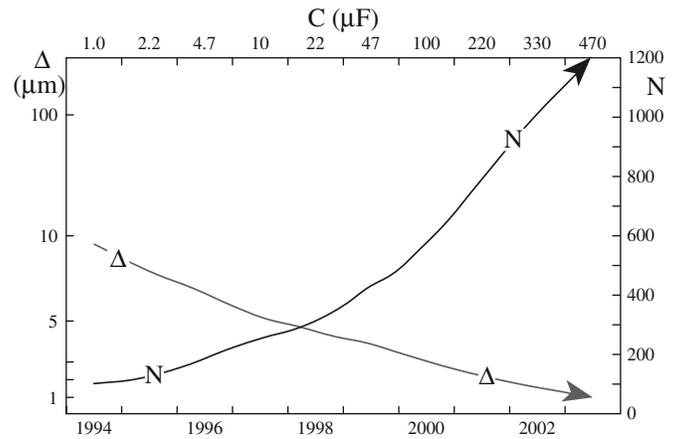FIGURE 37.3 Multilayer ceramic capacitor-sized trends.

YAG LASERS

The first application for Nd-doped YAG lasers was in laser range finding. Nonmilitary applications include cutting, welding, and drilling of metals for the automobile industry and in medical and dental procedures.

worldwide. The Czochralski process, which we described in Chapter 29, is used to grow singles crystals of YAG. Typical growth conditions are pull rates of 0.4 mm/h at temperatures nearing 1900°C.

One of the most common dopants is Nd^{3+}, which substitutes for yttrium in the crystal lattice. Commercial Nd-doped YAG is regularly produced with Nd concentrations ranging between 0 and 1.5 substitutional percent (sub%) of yttrium sites; from the chemical formula $Y_{3-x}(Nd_x)Al_5O_{12}$, the substitutional percent Nd is given by $x/3$. For instance, 1.02 sub% Nd = 0.153 at% Nd. Few crystals beyond 1.5 sub% Nd are available commercially.

The goal for commercial suppliers is to grow highly doped, large-diameter crystals. Increasing the dopant concentration results in a higher absorption coefficient, lower fluorescence lifetime, and greater overall laser efficiency. However, raising the Nd concentration increases the frequency of cracking during growth as we showed in Figure 16.1. If fracture occurs during growth then the process must be halted, which results in significant loss of time as a single boule can take 2 months to grow.

One of the causes of fracture has been shown to be small regions of inhomogeneity in the crystal as shown in the transmission electron micrograph (TEM) image in Figure 37.5. The widely spaced fringes in the image are moiré fringes caused by interference of the electron beam as it passes through two lattices that have different lattice parameters. The particle shown in Figure 37.5 actually has a larger lattice parameter corresponding to a local Nd concentration of 2.768% compared to the matrix, which has an Nd concentration of 1.02% Nd. (There is also a very small misorientation between the particle and the matrix, which also affects the spacing of the moiré fringes.)
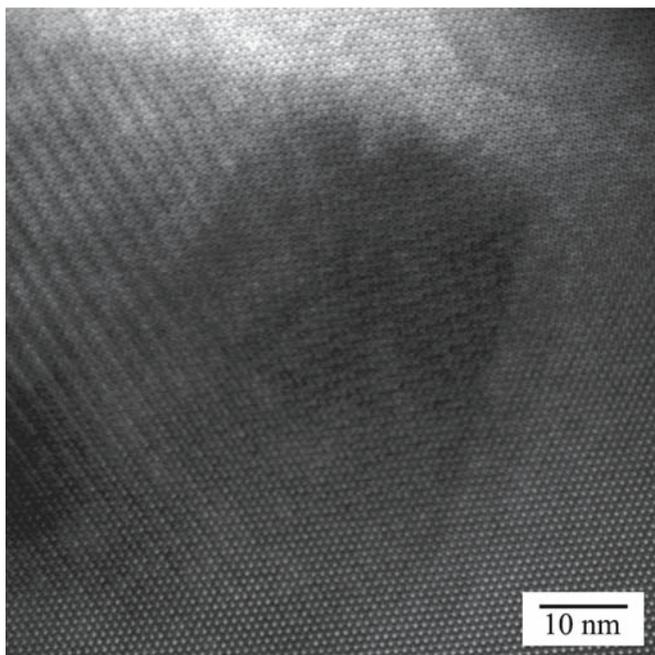
FIGURE 37.5 Moiré fringes spacing ~3 nm observed in a high-resolution TEM image of an Nd-rich particle in single-crystal YAG.

global nanoparticle market, which is dominated by ceramics, is now around $1 billion. Current applications for ceramic nanoparticles are summarized in Table 37.5.

- Electronic, magnetic, and optoelectronic applications account for 70%. The largest single use is slurries of abrasive silica particles (50–70 nm) for chemical/mechanical polishing (CMP).
- Biomedical, pharmaceutical, and cosmetic applications account for 18%. Sunscreens use nanosized powders of TiO_2 or ZnO.
- Energy, catalytic, and structural applications account for the remaining 12%. Uses include catalyst supports (e.g., for low-temperature H_2 production), ceramic membranes, fuel cells, and scratch-resistant coatings.

A recent example of the potential of nanosized ceramic powders in medicine is the demonstration that 5-nm cerium oxide (CeO_2) nanoparticles can prolong the life of brain cells. Usually these cells live for around 25 days in the laboratory, but after a low dose of the nanoparticles they have been shown to survive and function normally for 6 months. The hope is that this approach might one day be used to treat age-related disorders such as Alzheimer's disease. It was also found that the treated cells had increased protection against damage from ultra-violet (UV) radiation, as shown in Figure 37.6. The implication is that the nanoparticles mop up free radicals—reactive molecules that damage cells and are known to be involved in aging and inflammation.

An energy-related application undergoing extensive testing is the use of 10-nm CeO_2 particles as additives to diesel fuel. The CeO_2 nanoparticles catalyze the combustion of the fuel. The claim is that they release oxygen to oxidize carbon monoxide and hydrocarbon gases to carbon dioxide, and also reduce quantities of harmful nitrogen oxides. The result is a cleaner burning fuel that converts more fuel to carbon dioxide, produces less noxious exhaust, and deposits less carbon on the engine walls.

The market for nanosized powders is much smaller than for conventional ceramic powders, but the cost per kilogram is much higher. Despite progress in scaling up production and reducing costs, nanosized powders remain relatively expensive (often 100 times more than conventional ceramic powders).

There are growing concerns about the impact of nanoparticles on human health and the environment. Inhaling fine quartz particles is known to cause silicosis, a potentially fatal scarring of delicate lung tissue. Fine particles shed from hip and knee replacements as they wear cause

More recently there has been interest in using nanopowders to make polycrystalline laser hosts. These would avoid the need to use slow single crystal growth methods. The problem is keeping the grain size small enough during sintering to maintain transparency.

37.5 EMERGING AREAS

The topic of advanced ceramics is exciting as technologies developed in research laboratories and universities become adopted by industry. This market segment shows continued growth offering good employment opportunities for MS&E graduates.

In this section we will describe three emerging areas: ceramic nanopowders, high-temperature superconductors, and ceramic–matrix composites.

Ceramic Nanopowders

Nanotechnology is a "hot" research topic. The field is trendy, popular, and high-tech. Although silica and iron oxide nanoparticles have a commercial history spanning half a century or more it is really only within the plast 15–20 years that technologies have been developed for producing ultrapure nanosized powders of a range of ceramics. The

TABLE 37.5 Current and Emerging Applications for Nanosized Powders

Electronic, optoelectronic, magnetic applications	Biomedical, pharmaceutical, cosmetic applications	Energy, catalytic, structural applications
Chemical-mechanical polishing (CMR) supports	Antimicrobials	Automotive catalyst
Electroconductive coatings	Biodetection and labeling	Ceramic membranes
Magnetic fluid seals	Biomagnetic separations	Fuel cells
Magnetic-recording media	Drug delivery	Photocatalysts
Multilayer ceramic capacitors	MRI contrast agents	Propellants
	Orthopedics	Scratch-resistant coatings
Optical fibers	Sunscreens	Structural ceramics
Phosphors		Thermal spray coatings
Quantum optical devices		
Solar cells		

inflammation of the surrounding tissues and may result in the implant having to be replaced. Studies in which carbon nanotubes were placed directly into the lungs of mice showed that there was significant damage to the lung tissue. Because many of the potential applications for nanoparticles are in the human body it is important to determine their safety. It is also necessary to evaluate their environmental impact.

High-Temperature Superconductors

One of the benefits of increasing T_c above 77 K is that liquid nitrogen rather than liquid helium can be used as the coolant. Liquid nitrogen is both cheaper and more readily available than liquid helium. You will find the cost of liquid nitrogen described as either less than milk or less than cheap beer! The cost of liquid helium is often likened to fine champagne.

Soon after the discovery of high-temperature superconductors (HTSC) and, in particular, the YBCO compound there were grand predictions that these materials would revolutionize areas such as a high-speed transporta-

FIGURE 37.6 Effect of nanosized cerium oxide particles on the life of rat neurons.

tion and power transmission. The applications to date have been a little more modest. Magnetic levitation (maglev) for highspeed transportation has not been achieved with HTSC, but continues to a limited extent with the use of low-temperature materials. The other major application proposed for HTSC was in power transmission. However, due to the high cost and impracticality of cooling miles of superconducting wire, this has happened only with short "test runs." In May 2001 about 150,000 residents of Copenhagen, Denmark began receiving their electricity through superconducting cables. The superconductor chosen for this application was BSCCO (see Section 7.16) in the form of a tape wrapped around a flexible duct that carries the liquid N_2. The remainder of the cable consists of thermal and electrical insulation. In November 2001 commercial power was delivered to about 30,000 homes in Detroit, Michigan using a similar approach.

One area in which HTSC is poised to make a significant impact is in filters that improve network performance between wireless (cellular) devices and cell sites. Superconductivity avoids a typical trade-off by filtering out interference from adjacent signal bands without hindering the base station's ability to pick up weak signals. This market could be a $10 billion business by 2011.

According to estimates by the European Conectus consortium the worldwide market for HTSC products is projected to grow to about $5 billion by 2010 and to almost $40 billion by 2020.

Ceramic–Matrix Composites

Ceramic–matrix composites (CMCs) are being developed to provide an alternative to single-phase ceramic components because of the possibility of designing with higher toughness. The most important CMCs will probably be those with continuous fiber reinforcement. We described some of the processing routes in Chapter 20. Ceramic–matrix composites are at a relatively early stage of development compared to polymer–matrix composites (PMCs) and metal–matrix composites (MMCs) and significant research is needed if they are to meet their full potential. Table 37.6 lists some of the priorities.
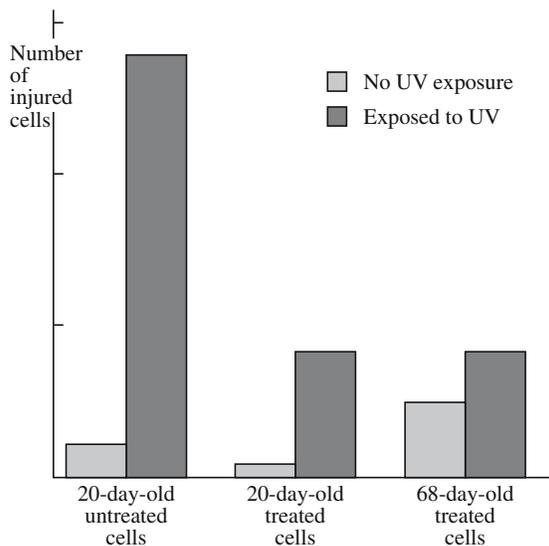
TABLE 37.6 Priority Needs in CMCs to Address Key Challenges Faced by Ceramic Manufacturers and End Users

Key Challenges for CMCs	Priority needs to address the challenge
Reduce the cost of precursors	Scale-up/cost reduction of fiber manufacturing
	Lower-cost interface materials and deposition processes
Improve understanding of failure modes	Basic understanding of interactions between CMC constituents and application environments
	Micro- and macromechanics understanding of interactions of CMC with an applied stress or strain
Increase temperature stability to 1200–1500°C	Higher-temperature fibers, matrix materials, and interface coatings
	Environmental barrier coatings (EBCs)
	Active cooling designs
Manufacturing scale-up and cost reduction	Larger furnace design and construction
	Automation/semiautomation of preform fabrication
	Low-cost tooling
	Near-net-shape fabrication
	Low-cost in-process and postprocess quality assurance

- *Cost*: Nonoxide fibers cost thousands of dollars per kilogram. Oxide fibers, even those that have been commercially available for years, sell for hundreds of dollars per kilogram. The main reason is that production volumes are small. Most fiber-reinforced CMCs utilize a layer between the fiber and matrix to optimize mechanical properties. The methods used for depositing this layer tend to be expensive and difficult to scale up for production.
- *Understanding Failure Modes*: We generally want a weak fiber–matrix interface in CMCs. A propagating crack is deflected around the fibers as shown in Figure 37.7 and does not propagate through the fibers. This
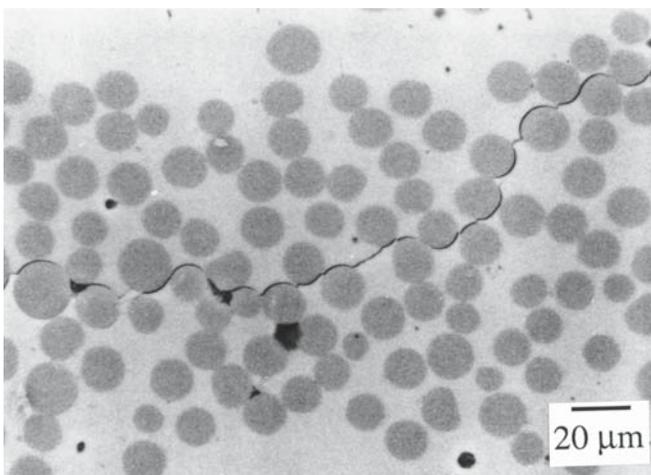

FIGURE 37.7 Crack propagation through a fiber-reinforced composite: SiC fiber in calcium aluminosilicate glass.

situation is opposite to that in PMCs where we often want a strong interface so that the load is transferred to the stronger fibers.

- *Increase Temperature Stability*: Fiber-reinforced CMCs have been demonstrated to survive in the severe environment of a gas turbine engine for 2500 hours at temperatures up to 1200°C. The use of environmental barrier coatings (EBCs) such as oxide layers on SiC appears to help extend durability, but more research is needed to determine whether they present a long-term solution.
- *Scale-up*: The high price of finished components made from fiber-reinforced CMCs is a major limitation. Reducing materials costs and increasing production volume would reduce costs substantially. One of the requirements for large-scale manufacturing of CMCs is the development of quick and inexpensive quality control procedures that can be used during production. The main processing defects are voids, density variations, and cracks. X-ray computed tomography (CT) is a powerful technique for this type of investigation and high-resolution detectors can detect defects and resolve features as small as 5 μm (see Chapter 10). But the technique remains expensive and slow and is not suitable at the present time for in-line process control.

Ceramics as the Enabling Materials

As you have realized from the discussion of capacitors, glass, data storage, etc., ceramic materials are often the critical part of a program or product even if the consumer never sees them.

Sapphire single crystals are grown for use in substrates, as windows, as IR-transparent domes, in jewel bearings, and as the "glass" on your best watch, but there are other applications of these and other single crystals that most of us never see. Large sapphire crystals are being tested for use in the LIGO Fabry-Perot interferometer. The aim of LIGO (laser interferometer gravitational-wave observatory) is to study astrophysical gravitational waves. There are two LIGO sites, one in eastern Washington and one in Louisiana. Sapphire should reduce the thermal noise compared to the fused silica that was initially used. The LIGO requires the crystals to be 35 cm in diameter and 12 cm long and uses 5N-pure alumina powder. The factors studied in assessing the sapphire mirrors for future generations of LIGO include all aspects of the influence of temperature on mechanical properties and the results are compared with the current fused-silica mirrors. In either case, the ceramic is the enabling material and is the topic of very focused research.

37.6 MINING

From the ugliness of an open cast mine, to the health problems of mine workers, to the bitter civil wars fought over mineral resources in Africa, the impact of mining

and our search for raw materials are frequent topics in the news media. Many of the ceramic products we use are produced from natural resources. For example, the main component of most glasses is SiO_2, which comes from sand. The main component of traditional ceramic products like tableware and bricks is clay, which is available in different grades and is usually extracted by opencast mining. These raw materials are abundant and widespread.

Talc

A mineral that has caught the attention of environmentalists and conservationists is talc. Talc is used in the production of paper and tiles, and as coatings in the motor industry for dashboards and fenders (bumpers). However, its main use is in beauty products such as eye shadow, lipstick, body lotions, deodorants, and soaps. Talc is produced from soapstone, which occurs in the form of large subsurface boulders. The concern is that some of the finest powder is obtained from soapstone that is the result of illegal mining in India's Jamwa Ramgarh Wildlife Sanctuary and the neighboring Sariska Tiger Reserve 250 km southwest of Delhi. These sites are considered essential to the revival of the Indian tiger. The current population of Indian tigers is about 3000, but they are threatened with extinction because of the loss of habitat and prey caused by the mining activities.

Tantalite

The dielectric in tantalum electrolytic capacitors is tantalum pentoxide (Ta_2O_5), which forms as a thin layer on tantalum as illustrated in Figure 37.8. The benefits of using tantalum capacitors are that they are small, have a

wide operating temperature range (−55°C to 125°C), and are very reliable.

Controversy has arisen recently concerning the source of tantalum: the mineral tantalite, which is found in association with niobium as the ore columbite-tantalite or col-tan. A major supply of col-tan is found in the Kahuzi-Biéga Park in the Democratic Republic of Congo. The park is home to the eastern lowland gorilla, one of the rarest animals in the world. As a result of col-tan mining the gorilla population is being decimated and the billion-dollar export has funded the Congo's civil war.

37.7 RECYCLING

There are three basic reasons given for recycling:

1. Preserve finite resources
2. Protect the environment
3. Save energy

The raw materials used for glass production are abundant and unlike many metal ores are not in any imminent danger of being depleted. But producing glass does involve consumption of large amounts of energy as shown in Table 37.7. (Glass is the lowest on this list because high-purity sources of SiO_2 are readily available.) Table 37.8 shows the total energy involved in producing a 12-oz beverage bottle including factors such as mining and transportation.
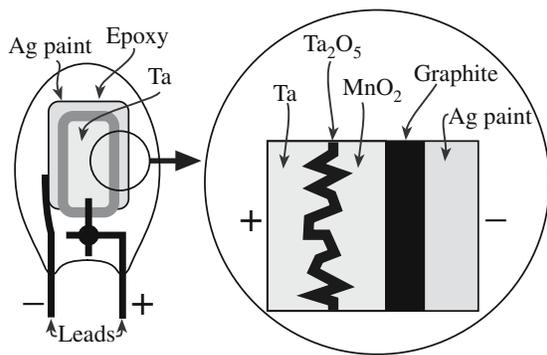

FIGURE 37.8 Schematic diagram of the structure of a solid electrolyte Ta capacitor.

TABLE 37.7 Energy Consumption to Extract 1 ton of Raw Material from Its Ore or Source

Material	Energy (GJ)
Aluminum	238
Plastics	100
Zinc	70
Steel	50
Glass	20

TABLE 37.8 Energy Consumption per Use for a 12-oz Beverage Container

Container	Energy (MJ)
Aluminum can used once	7.4
Glass bottle used once	3.9
Recycled aluminum can	2.7
Recycled glass bottle	2.7
Refillable glass bottle used 10 times	0.6

The energy savings by recycling and reusing glass containers are also shown in Table 37.8.

Glass recycling has been going on for thousands of years; broken glass was reused in antiquity to make new glass objects. This ancient recycling system makes it difficult for archeologists to determine the provenance of a glass object from its chemical composition alone. A structured recycling program for domestic glass waste started in 1975 and was initiated by the glassmaking companies.

In Chapter 26 we described the glass-forming process. The initial step is that the batch, which consists primarily of sand, is melted. The temperature required varies with the composition of the batch, but is typically in the range of 1300–1600°C. Adding crushed recycled glass, called cullet, to the melt promotes melting of the sand permitting the use of reduced furnace temperatures with considerable savings in both raw materials and energy. For example, if a glass batch for beverage container glass contains 25% cullet it requires 5% less energy to melt. Although cullet has been used in ratios ranging from 0 to 100% of the glass, 30–60% cullet is the most effective range. For colored bottles cullet comprises about 50% of the batch.

One difficulty associated with using recycled glass, particularly from consumer recycling, is the necessity to sort the discarded bottles according to color. In the United States over 65% of container glass is clear, 25% is brown or "amber," and 10% comes in different shades of green and occasional blue and other colors. These percentages do not correspond exactly to the glass contents in domestic waste because of the consumption of imported beverages that come in mostly brown and green bottles. In France, 80% of the glass containers are green. Wine is usually packed in green bottles because it provides better UV protection, but the original reason is that when the wine bottle was invented in England during the seventeenth century it was made of green glass.

Clear glass is the most valuable glass for recycling. Both clear and brown glasses are very sensitive to impurities so they cannot be mixed with each other or with other types of glass. Green glass, however, can accept other glass types without noticeable influence on the color. However, green glass is often the most difficult for the glass manufacturers to use simply because the supply of recycled green glass often exceeds the demand. One application for recycled green glass that is not influenced by color is for fiberglass insulation.

GLASS RECYCLING: FACTS AND FIGURES

More than 40 billion glass containers are produced each year in the United States.

All glass food and beverage containers can be recycled.

Recycling a glass jar saves enough energy to light a 100-W light bulb for 4 hours.

Glass constitutes about 6% of U.S. municipal solid waste.

Approximately 12 million tons of waste glass food and beverage containers are generated each year in the United States.

About 25% of all glass food and beverage containers are recycled in the United States.

The average glass bottle contains over 25% recycled glass.

It is important that container glass is not mixed with other types of glass product such as windows, light bulbs, mirrors, and tableware. These glasses have different compositions as we showed in Chapter 26. Because of problems associated with contamination of recycled glass the use of returnable/refillable glass bottles and containers is increasing. Switching to refillable containers can save up to 56% of the energy consumed, reduce water consumption by up to 82%, and decrease materials consumption over 10 times for 35 refills.

Currently the cost of recycling far outweighs the value of the recyclables. It may take up to five times the amount of money a recyclable product is worth to collect, process, and transport it to a buyer. As a result, the recycling industry is currently driven by consumer demand, not by profit. Many environmental economists point out that in a "sustainable" economic system (one based on the real costs to the environment resulting from the transportation and production of goods and materials), recycling is financially cost effective. In such a system, the prices of products made from virgin materials would be prohibitive, encouraging manufacturers to use recycled materials instead. However, under such a system, the concept of curbside recycling would become even less cost effective than it is now, due to increasing transportation and energy costs.

Some of the issues that drive the need for recycling in Europe are quite different from those in the United States. One significant difference is population density. Recycling in the Netherlands, which recycles more than 80% of its glass waste, is much more important than in the United States. The population densities are about 372 inhabitants/km^2 and 27 inhabitants/km^2, respectively. As the population density increases, the landfilling of waste, particularly industrial waste, becomes more difficult and unacceptable for the nearby population. Landfill space has to compete with the land requirements for expanding suburban developments and in many cases agricultural land as well.

One recycling issue that is important throughout the developed world is what to do with the approximately 300 million TVs and computer monitors that are thrown out each year. The European Union Waste Electrical and Electronic Equipment Directive have banned them from being dumped in landfills because the screens contain PbO added to shield against the X-ray radiation released by the high anode voltage. Table 37.9 shows typical compositions of cathode ray tube (CRT) glasses.

TABLE 37.9 Some Typical Chemical Compositions of CRT Glasses (wt%)

Oxide	Color TV panel	Color PC panel	Color TV funnel	PC funnel
Na_2O	8.0–8.6	6.6	6.3–6.8	5.45
K_2O	7.0–7.5	7.3	7.8–9.7	8.05
MgO	0.2–1.3	0.33	1.0–1.8	1.5
CaO	0.5–2.5	1.15	1.4–3.8	3.5
SrO	1.5–8.5	8.65	0.15–0.5	0.5
BaO	10–12	1.15	1.0–1.95	3.5
Al_2O_3	2.2–3.2	2.05	3.0–4.0	3.6
ZrO_2	0.2–1.5	0.95	0.08	0.1
PbO	0.0–0.1	0.05	14.7–22.7	20.25
SiO_2	60–62	59	52–59	53
CeO_2	0.25	—	—	—
TiO_2	0.4	0.6	0.05	0.07
Sb_2O_3	0.25	0.5	0.05	—
As_2O_3	0.02	0.02	0.01	—
Fe_2O_3	0.07	0.12	0.06	—
ZnO	—	0.6	—	0.06

To prevent a growing mountain of TVs one of the plans is to melt down the tubes in a sealed furnace under conditions that would reduce the PbO to Pb. The heavy molten metal would run out of fissures at the base of the furnace, but the molten glass will be retained. The purified glass could then be used for other applications, such as bottles.

The use of recycled glass as an ingredient in concrete is being explored in several locations worldwide.

37.8 IN THE NUCLEAR INDUSTRY

Uranium dioxide (UO_2) has been important as a nuclear fuel since the mid-1950s and is obtained from its major ore, uraninite. After leaching the ore, U_3O_8 is precipitated out. The average price for U_3O_8 is about \$25/kg and the United States used about 24 million kg of U_3O_8 last year. Before use in a nuclear reactor U_3O_8 is converted into UF_6 gas. Then using either diffusion or centrifugal processing, $U^{235}F_6$ is separated from $U^{238}F_6$. The U^{235}-enriched gas is reacted to form UO_2 powder, which is pressed into pellets. These pellets are loaded into zirconium alloy tubes making the fuel rods. A 1000-MW reactor will "burn" 25 t of UO_2 per year, and 1 kg of fuel costs about \$900. Thus, a 1000-MW reactor will consume about \$22.5 million of UO_2 annually.

In the United States there are presently about 100 operable nuclear reactors (over 400 worldwide) producing 21% of the country's electrical power. The number of operable reactors has decreased since it reached its peak in 1990, but there is some interest in reviving the nuclear industry because it is a zero "greenhouse emission" technology and because it does not consume limited resources of fossil fuels.

One of the major problems with increasing nuclear reactor capacity is what to do with the spent fuel. There are two current approaches:

- Reprocessing (adopted by UK, France, Germany, Japan, China, and India)
- Storage (adopted by the United States, Canada, and Sweden)

In Europe, spent fuel is frequently reprocessed, which involves dissolving the fuel elements in nitric acid. Since plutonium is created in the fission process, reprocessed fuel contains both radioactive U and Pu, and is referred to as a mixed oxide (MOX) fuel.

The remaining liquid after Pu and U are removed is high-level waste (HLW), containing about 3% of the spent fuel. It is highly radioactive and continues to generate a lot of heat. This waste must be immobilized and because of the presence of radioisotopes with long half-lives it must be immobilized for tens of thousands of years. Ceramics are key materials in this process.

The following are major requirements for waste immobilization:

- The radioactive elements must become immobilized in the crystal or glass structure.
- The leaching rate of radioactive elements must be low.
- The cost must be acceptable.

The main method of solidifying HLW, not already contained in spent fuel rods, is to "vitrify" it into a borosilicate glass and cast it into stainless steel cans for ultimate burial. Vitrification of civil HLW first took place on an industrial scale in France in 1978. A year's worth of HLW from a 1000-MW reactor can be stored in about $26 m^3$.

A second-generation immobilization material, "synroc," is in development. This synthetic rock, based on mixed titanate phases such as zirconolite, hollandite, or perovskite, incorporates the HLW elements into its crystal structure, yielding excellent chemical stability. Synroc features leach rates more than an order of magnitude lower than borosilicate glass.

Whether the final HLW is vitrified material from reprocessing or entire spent fuel assemblies, it eventually needs to be disposed of safely. This means that it should not require any ongoing management after disposal. While final disposal of HLW will not take place for some years, preparations are being made for sites for long-term disposal. One of these is Yucca Mountain in Nevada.

37.9 PRODUCING AND STORING HYDROGEN

Thermochemical Processing

We know it is completely feasible to produce hydrogen using solar energy from the point of view of thermodynamics. The idea is to use thermochemical processing.

The goal is to convert water (in the form of steam) into its components, hydrogen and oxygen, and then to collect the hydrogen for use as a fuel. It is simple! The process is particularly exciting because efficiencies of up to 76% should be achievable, which makes it both commercially and environmentally very attractive.

The principle behind the process is to use solar energy to drive a highly endothermic reaction and then produce hydrogen by a subsequent exothermic reaction. This is known as a *two-step water-splitting cycle*. Solar energy in the form of heat is used to reduce the ceramic (a metal oxide); this reduced metal oxide is then reoxidized by removing the oxygen from water, thus producing hydrogen gas. The reduced (lower valence) metal oxide in step I (thermal reduction) could alternatively be a metal carbide, a metal nitride, or even a metal. The second step (oxidation by water) is known as hydrolysis. The limit for step I would be

Step I: metal oxide → reduced metal oxide + O_2
Step II: reduced metal oxide + H_2O → metal oxide + $2H_2$

$$M_xO_y \rightarrow xM + \frac{y}{2}O_2$$
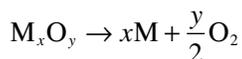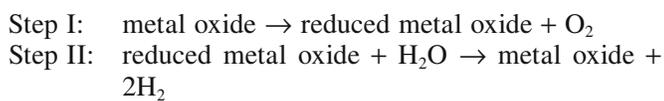
If we use FeO in step I, then the temperature must be >1600 K. However, step II is then spontaneous at a temperature of ~1200 K.

Several systems are being explored for this purpose. These include the reduction of ZnO (in some cases enhanced by the presence of C), the reduction of ceria, and the reduction of oxides containing Fe^{3+} (both iron oxide and a range of ferrites).

All that we need to do is to optimize the ceramics and, perhaps the more challenging step, optimize the geometry of the sample to allow repeated cycling (1) without degradation and (2) while allowing easy extraction of the hydrogen. So the usual process is to improve the design (tailor) of both the material (e.g., powder versus multilayer films or foams) and of the reactor itself.

This whole process should remind you of our discussion of phase boundaries (PBs) in Chapter 15 and reactions in Chapter 25. The solar part of this has many similarities to processes that are now being explored for producing lime (the endothermic calcinations of $CaCO_3$) and other ceramics. Currently we use fossil fuels to produce cement and lime, which account for 5% and 1%, respectively, of the global human-made CO_2 emissions—up to 40% of this is from burning the fossil fuels.

Proton Exchange Membrane Fuel Cells

High purity hydrogen is needed for use in proton exchange membrane (PEM) fuel cells. Hydrogen is currently produced industrially (9 Mt per year in the United States) through steam reforming of natural gas. Alternative fossil fuel hydrogen technologies are needed. Coal is a potential

TABLE 37.10 Catalytic Properties of Mo Carbide for Fuel Reforming Applications

Reactivity	Other important catalytic properties
Similar reactivity to Pt in alcohol synthesis, methane dehydrogenation, and hydrocarbon isomerization	High resistance to coking even under stoichiometric fuel reforming conditions
Excellent hydrodesulfurization activity	Shows the potential of being sulfur-tolerant
Promotes the water gas shift (WGS) reaction at low temperatures	High selectivity for hydrocarbon conversions

source of energy for hydrogen production but is more challenging because it is dirty. Abraham Darby I realized the problems with coal in the early eighteenth century, which led to his use of coke (a high purity form of carbon) for smelting iron. This process allowed the expansion of the iron trade.

Catalysts required for reforming of coal into hydrogen must be resistant to poisoning by contaminants. Current catalysts are based on expensive precious metals, mainly platinum. A possible low-cost alternative is molybdenum carbide. Molybdenum carbide is one of the more widely studied carbide systems and has shown useful catalytic properties for fuel reforming applications, which are summarized in Table 37.10.

The stable phase is β-Mo_2C and there are several non-stoichiometric high-temperature phases MoC_{1-x}, with both hexagonal and cubic structures. Nanoparticles of molybdenum carbide seem to be most effective for catalysis because of their large surface areas (up to 200 m²/g). Catalyst nanoparticles about 10 nm in diameter are formed on various supports such as Al_2O_3, ZrO_2, and even carbon nanotubes. It is important to prevent the particles from oxidizing because MoO_2 is inactive for fuel reforming.

Hydrogen Storage

Of all the limitations preventing the achievement of the hydrogen economy the most significant is hydrogen storage. For transportation applications storage requirements are particularly stringent and none of the current approaches comes close to meeting targets. Indeed some of the approaches are actually dangerous. Storing hydrogen on the surface of nanomaterials is an exciting possibility. The idea is again to use the very large surface areas available at the nanoscale. The hydrogen attaches nondissociatively (i.e., as H_2) through weak molecular-surface interactions such as van der Waals forces. Studies have shown that hydrogen will attach to the surface of carbon nanotubes, but the temperatures do not seem to be ideal for transportation needs. Recently, using glasses for hydrogen storage has been proposed and experimentally
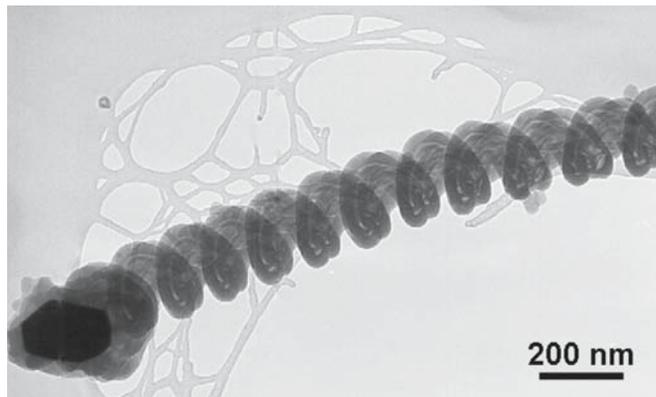
FIGURE 37.9 TEM image of silica nanoropes for hydrogen storage (on a lacy C film).

FIGURE 37.10 Looking through two ceramic extruded cordierite honeycomb substrates for catalytic converters.

hydrogen has been shown to attach to the surface of two-dimensional silica glass nanostructures (e.g., wires, ropes, and springs) at room temperature and be released at ~100°C. Figure 37.9 shows a TEM image of silica nanoropes. The only difference, apart from size, between these nanostructures and "bulk" glass fibers appears to be that the surface is more ionic, which may be important for hydrogen attachment. The nanoropes grow by the vapor–liquid–solid (VLS) mechanism described in Chapter 29. The Au catalyst is the dark particle. The deposition process occurs at temperatures as low as 300°C allowing them to be formed on polymer substrates.

37.10 AS GREEN MATERIALS

Catalytic Converters

Catalytic converters are used in the exhaust system of automobiles and can reduce emissions of carbon monoxide and hydrocarbons by up to 90%. Carbon monoxide can be transformed into carbon dioxide, and unburned hydrocarbons from the fuel get burned on the metal surfaces. Nitric oxide, one of the main contributors to urban smog, will react with carbon monoxide to form carbon dioxide and nitrogen gas. These processes are conducted in catalytic converters.

The first catalytic converters used mainly platinum, but palladium is now the predominant catalyst metal. Sixty percent of the palladium manufactured worldwide is used in catalytic converters. Other uses are as the electrodes in MLCCs and other electronic components, and a small amount is used in jewelry (for example, an alloying element in white gold).

The metal is dispersed as tiny particles on a supporting framework of a porous ceramic. Because of the need for thermal
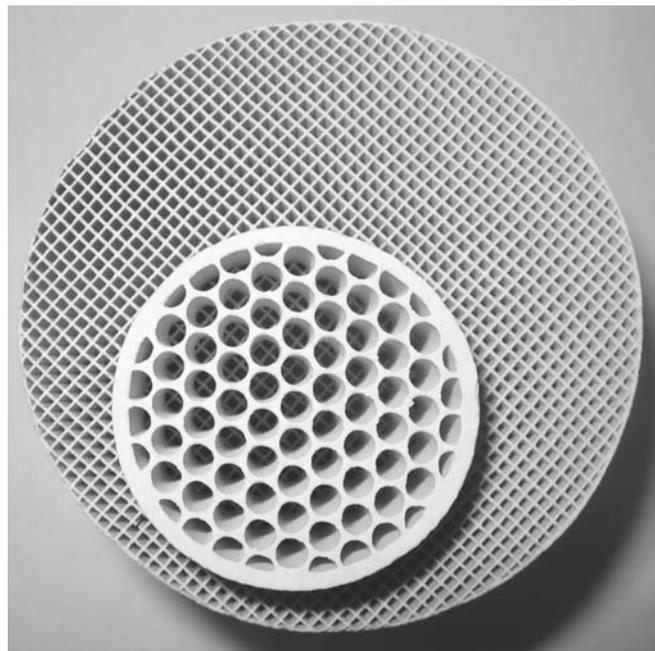
shock resistance a ceramic with a near-zero coefficient of thermal expansion is required. One such material is cordierite. Figure 37.10 shows an example of a ceramic honeycomb substrate for a catalytic converter. Substrates have been produced with up to 900 cells per square inch and walls of thickness of 50 μm. These complex shapes are produced by extrusion, a process we described in Chapter 23. The ceramic powder is mixed with a hydraulic-setting polyurethane resin. The mix is extruded into a water bath at a rate of about 2 mm/s. The extrusion rate matches the rate at which the resin cures.

Other requirements for the catalyst substrate are

- Low cost
- Thermal-mechanical durability
- Lightweight

Photoelectrochemical Solar Cells

Photoelectrochemical (PEC) solar cells use a hybrid structure consisting of inorganic semiconductors and organic molecules. There are several different geometries. The one shown in Figure 37.11 uses a film of sintered TiO_2 nanoparticles (10–30 nm) on a conducting glass substrate. Dye molecules that absorb sunlight are coated onto the TiO_2 particles. The TiO_2 itself does not absorb a significant amount of

CATALYTIC CONVERTERS
These have reduced automobile pollution by more than 1.5 billion tons since 1974.
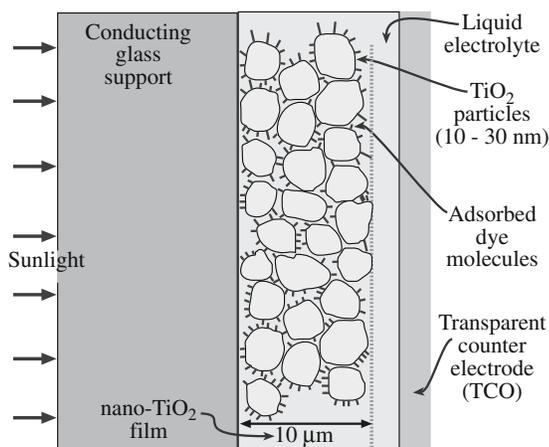
FIGURE 37.11 Schematic of a dye-sensitized nanocrystalline solar cell.

sunlight; it is a wide-band-gap semiconductor ($E_g = 3.0\,\text{eV}$). The dye molecules absorb by electrons moving into excited states. These excited electrons are injected into the TiO_2, which creates positively charged dye molecules. The incident solar energy has created electron–hole pairs. If these pairs are separated then we have a photovoltaic (or solar) cell. The circuit is completed by a liquid electrolyte and transparent electrode. Despite the high efficiencies of PEC solar cells, the lifetime of the photoelectrode and the high cost have restricted commercialization.

CHAPTER SUMMARY

In this chapter we described some of the industrial aspects of ceramics. Ceramics make money. Unfortunately obtaining the raw materials can have some undesirable environmental and societal impacts. The environmental impact of nanomaterials is an issue that has not yet significantly concerned the ceramics industry because no one knows exactly what that impact is. But as the market for ceramic nanopowders and other nanostructures (such as wires and tubes) increases the environmental concerns will have to be addressed. Many of the "grand challenges" we face as a society, such as energy, the environment, and health care, will require innovative technological solutions. Ceramics can play an important role in these areas, e.g., nuclear waste immobilization, catalytic conversion, and viral nanosensors.

It is important to realize that industry is constantly in a state of flux so numbers reported here can change from year to year. Also this chapter reflects a snapshot of an industry at the beginning of the twenty-first century. In a decade, the relative importance of some of the topics we described may have increased, decreased, or disappeared altogether.

PEOPLE IN HISTORY

Darby, Abraham I (1678–1717) was born in Staffordshire; he patented sand casting in 1708 and invented coke smelting in 1709.

Feynman, Richard (1918–1988). The beginning of research in nanotechnology can be traced back to a visionary talk given by Feynman in 1959 titled "There's Plenty of Room at the Bottom." Since then nanotechnology has captured the minds and imaginations of many scientists and engineers. A transcript of his nanotechnology talk can be found at http://www.zyvex.com/nanotech/feynman.html. Feynman won the 1965 Nobel Prize in Physics.

Wollaston, William Hyde (1766–1828) was an English scientist who discovered Pd in 1803 and named it after the asteroid Pallas, found in 1802. The mineral wollastonite is named after him.

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WWW

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www.kitco.com

Precious metal prices and historical trends.

www.nulifeglass.com

NuLife Glass of Wilmslow in Cheshire. A company that plans to recycle the glass used in TV and computer screens.

www.kemet.com

KEMET Corporation in Greenville, South Carolina is the largest manufacturer of solid tantalum capacitors and the fourth largest manufacturer of MLCCs in the world.

www.conectus.org

The European superconductivity consortium.

Company sites that make some of the products we mention in this chapter:

www.oxonica.com

Oxonica website. You can find out about the status of the nanoparticle fuel efficiency trials.

www.utilities.dteenergy.com

Detroit Edison website.

www.ceramicindustry.com

Ceramic Industry magazine. Also find out about the Giants of Ceramics.

NWT Diamond Industry

www.iti.gov.nt.ca/diamond/production.htm

for details on the Diavikmine.

EXERCISES

37.1 In addition to oxygen what other impurities might you expect in Si_3N_4 powder?

37.2 Why is the extent of Nd substitution in YAG so small?

37.3 What companies make the Pd–Ag metallization used for MLCCs?

37.4 Do TiO_2 and ZnO play different roles in sunscreen? Which is the better material for this purpose?

37.5 Describe one process used to make CeO_2 nanoparticles.

37.6 In the form of a table compare the cost of conventional (micrometer-sized) ceramic powders with the nano-sized equivalents.

37.7 How much glass is recycled in your community (or state)?

37.8 Compare the costs of recycling to landfilling for various materials.

37.9 Why is the BSCCO superconductor the material of choice for superconducting wires?

37.10 What is the current world capacity for reprocessing nuclear waste?