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Chapter 1

An Introduction to Materials Science

This chapter provides an overview of materials chemistry and some context for the concepts developed in subsequent chapters. The first part of this chapter articulates the interdisciplinary nature of materials chemistry and illustrates the roles of synthesis and processing in defining the properties of a material.

The second section of the chapter provides some perspective on the impact that materials have on our environment. A material's life cycle, comprising its origin, use, and disposal, is an increasingly important consideration in evaluating its utility. These issues are explored, using a now-recyclable industrial hydrodesulfurization catalyst as an example.

The final part of the chapter is meant to convey some of the excitement and relevance of modern materials chemistry. The Age of Materials is characterized by new analytical methods, including atomic-scale imaging; unprecedented chemical control of interfaces; and the purposeful design of new materials, even of “smart” materials that respond in predictable ways to stimuli. Some “high-tech” materials, those developed or produced with the aid of the latest technology, and advanced devices are already an integral part of our lives. The trajectory of the materials chemistry enterprise suggests that many more soon will be!

What Is Materials Science?

Materials chemistry is a broad, chemically oriented view of solids—how they are prepared and their physical and chemical characteristics and properties. Often, the term “materials science” is used to describe the understanding of solids that emerges from the combined viewpoints of

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chemistry, physics, and engineering, and, for biomaterials, the biological sciences.

Materials science has been represented by the tetrahedron shown in Figure 1.1 *(1)*. Each vertex of the pyramid is equally important in this holistic portrait of materials science: "synthesis and processing" refers to the preparative conditions that determine atomic structure and microstructure (the arrangement of micrometer-sized groups of atoms) of a material; "structure and composition" is the arrangement and identity of atoms derived from the particular synthetic conditions employed to prepare the material; "properties" refers to the characteristics (optical, mechanical, electrical, etc.) of the material; and "performance" represents the conditions under which the material maintains its desirable characteristics. Materials chemistry is the key to unifying this entire picture, a theme that will be presented in this overview chapter and reinforced throughout the text.

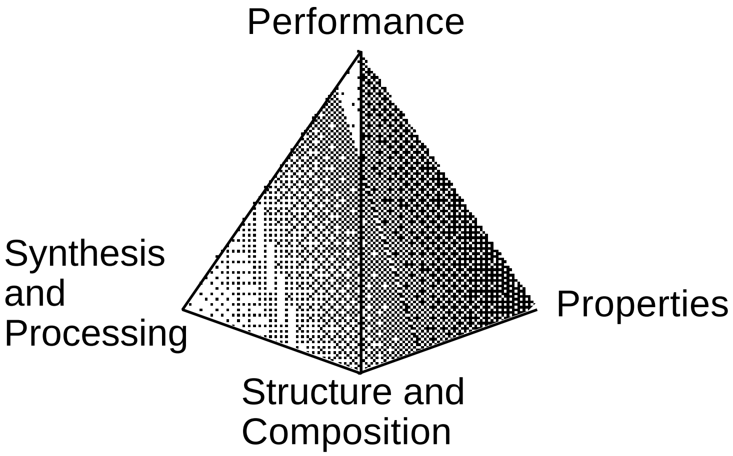
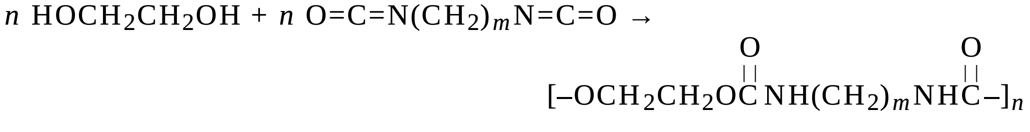


Figure 1.1. The materials tetrahedron.

A particularly striking example of materials chemistry that animates this tetrahedral interdependence is the behavior of polyurethane foam, pictured in Figure 1.2. Polyurethane is prepared as follows:



$$n\ \mathrm{HOCH_2CH_2OH} + n\ \mathrm{O{=}C{=}N(CH_2)}_m\mathrm{N{=}C{=}O} \rightarrow [-\mathrm{OCH_2CH_2O}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{NH(CH_2)}_m\mathrm{NH}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-]_n$$

The desirable features of the foam, for example, good long-term performance as a thermal insulator and as an air filter, are linked to the network of pores in the foam. In turn, the pore network reflects the degree of polymerization (the distribution of *n* values) and the microstructure of the polymer, both of which are controlled by the synthetic conditions employed.

Commercially available samples of polyurethane have a mechanical property that is typical of most materials commonly encountered: When opposite ends of the foam are pulled apart, placing the foam under tension, it becomes longer in the direction that it is pulled and constricts in the perpendicular directions (Figure 1.2A and 1.2B); a common rubber band provides another graphic example of this effect.[1]

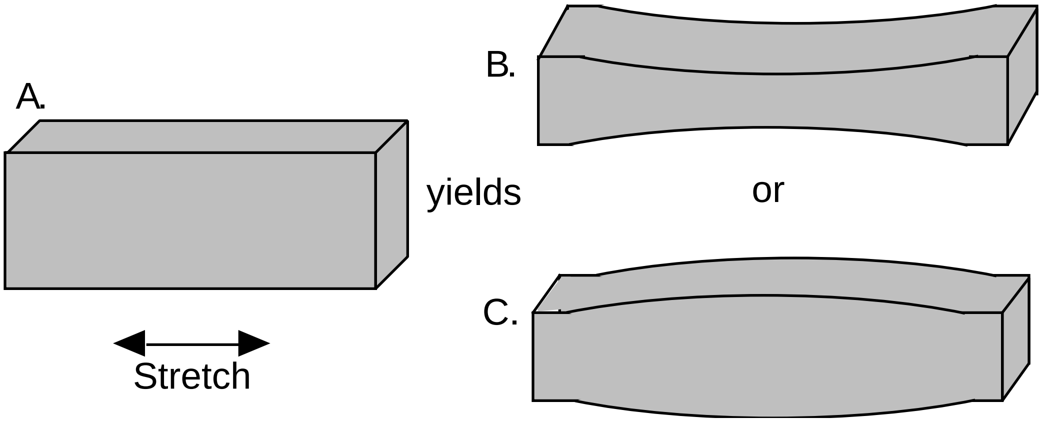


Figure 1.2. A block of polyurethane foam (A) will constrict (B) or bulge (C) in the middle when stretched, depending upon how it has been processed.

The importance of processing in materials chemistry is dramatically illustrated by converting this foam to so-called “re-entrant foam” *(2)*. If the polyurethane foam is compressed uniformly in all directions (isotropically) at a temperature of about 180 °C, below the melting point of the polymer, the applied pressure and heat can collapse the pores in the foam. Such a material will be substantially denser than it was before processing. Moreover, placing the pores under tension in one direction should cause them to expand in all directions, as sketched with the idealized pore shown in Figure 1.3. This expansion of the microstructure should result in a macroscopic expansion of the sample in all directions.

Figure 1.2C shows the realization of this prediction: when the re-entrant foam is stretched, it counterintuitively expands in the perpendicular directions as well! In the context of the materials tetrahedron, although the chemical composition of the solid remains unchanged, the processing step has increased the density of the solid, affected its microstructure, and completely altered the mechanical properties of the polymer.

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[1] Such materials are described as having a positive Poisson ratio. This ratio, often symbolized by μ (mu), is defined as

$$\mu = \frac{\text{fractional decrease in width}}{\text{fractional increase in length}} = \frac{\Delta w/w}{\Delta l/l}$$

As defined, the Poisson ratio is usually positive, reflecting the fact that the change in the width is negative (the width shrinks) as the length increases. A negative Poisson ratio indicates the opposite effect, a relatively unusual expansion of the width as the material is stretched.

Demonstration 1.1. Re-entrant Foam

Part A. Preparation of Re-entrant Foam
(This only needs to be done once; the samples can be reused.)

Materials

Low-density open-cell (filter) polyester or polyether polyurethane foam with 10 to 20 pores per inch. A convenient size is 1.5 × 1.5 × 6 inches. *See* Supplier Information.
Scissors
Aluminum foil
Drying oven

Procedure

- Trim the lengthwise edges of the foam with scissors in order to make the sample easier to roll.
- Compress a piece of foam lengthwise to about one-third or one-half of its length, and then compress it axially by the same amount while rolling it in a 1 foot × 1 foot piece of aluminum foil. To optimize the effect, the foam should be compressed isotropically (equally in all directions) by about a third to a half.
- Twist the foil ends to hold the foam in its compressed shape. Figure 1.4 shows a sample before and after compression in aluminum foil.
- Heat the foil-wrapped foam in an oven for about an hour at about 175–195 °C. Remove it from the oven and let the sample cool before opening.

Part B. The Effect of Processing

Materials

Thick rubber band that has been cut to be a flat strip
Untreated foam
Re-entrant foam

Procedure

- Place each material, in turn, on an overhead projector. Stretch each by pulling opposite ends of the material apart. The rubber band and the untreated foam will become thinner, but the re-entrant foam will become thicker in cross-section upon stretching.

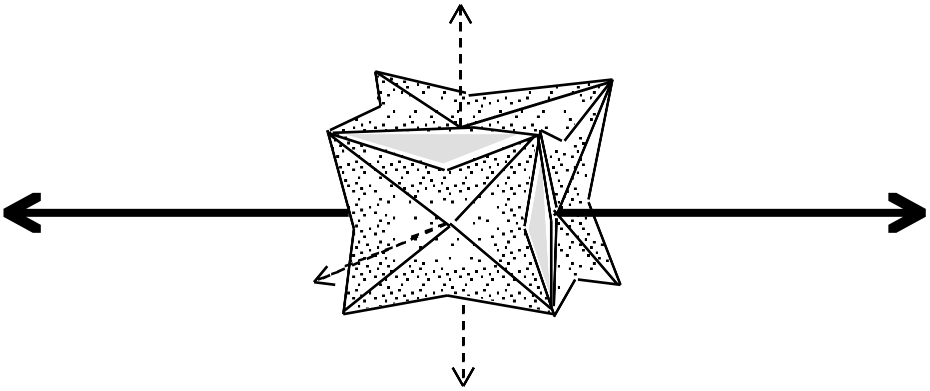

Figure 1.3. An idealized re-entrant pore, viewed as a cube with each of the six faces collapsed inward. After the appropriate processing, a stretching force applied in the horizontal direction (dark arrows) will cause the remaining four faces of the cube to expand (dashed arrows).

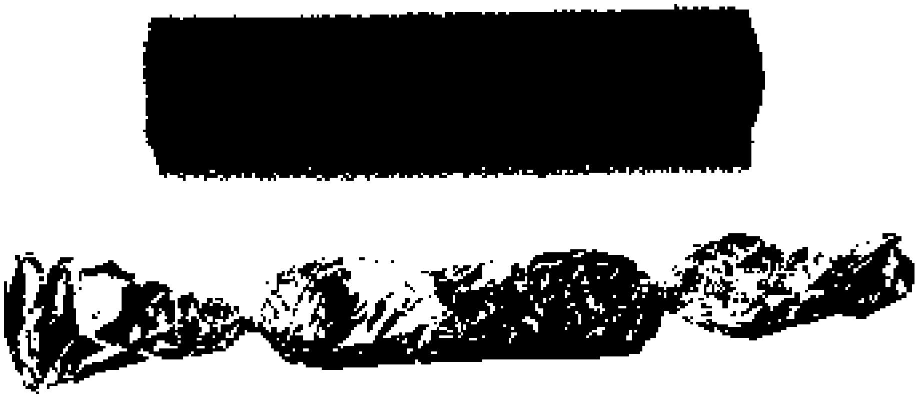

Figure 1.4. Untreated foam and the same sample compressed in aluminum foil for heating.

The Life Cycle of a Material

In preparing and using materials, the entire life cycle of a solid needs to be appreciated. Figure 1.5 shows a total materials cycle *(3)*, which begins with extracting raw materials for a targeted solid; continues with the synthesis and processing leading to the tailored material; passes on to the incorporation of the material into a deliverable product for a desired application; and ends with the fate of the waste derived from the material. In all steps of this cycle, energy costs and the effect on the environment need to be addressed. This kind of holistic thinking is rapidly becoming part of the culture of materials chemistry.

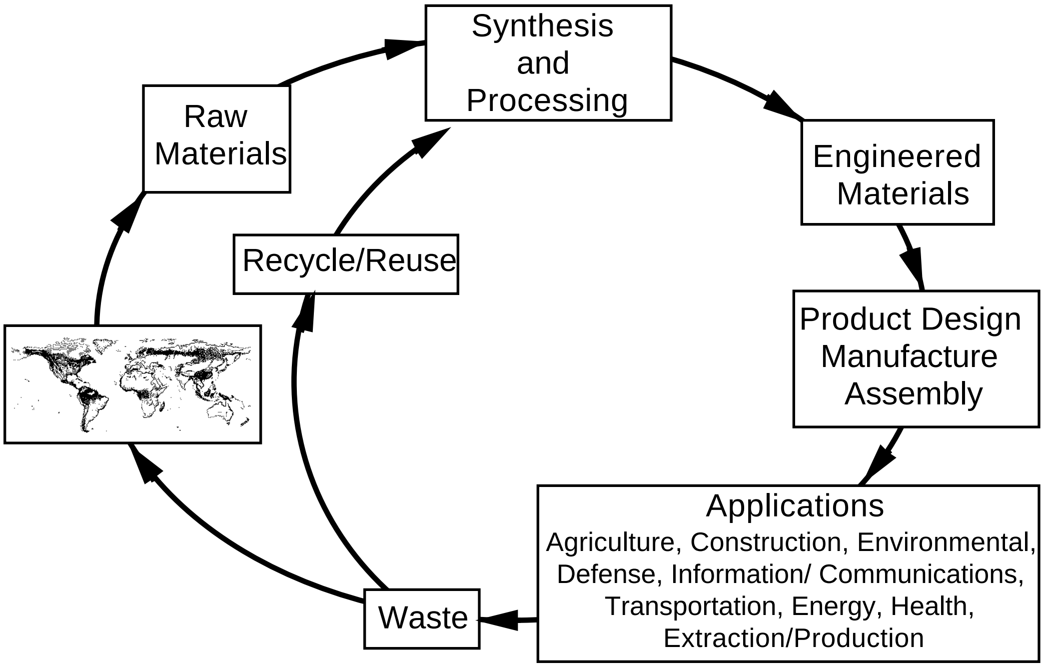

Figure 1.5. A total materials cycle. (Adapted from reference 3).

This cycle is illustrated better by looking at a specific example: the production and use of a catalyst for the hydrodesulfurization (HDS) process, a process for removing sulfur from petroleum feedstocks. If the sulfur is not removed before combustion of the petroleum, it contributes to acid rain. The typical catalyst used in the HDS process is MoS_2 supported on alumina; the activity of this catalyst is promoted by the addition of small amounts of cobalt. There is some dispute as to the exact chemical form of the cobalt, that is, whether it is present as the sulfide, Co_9S_8, or somehow more intimately connected with the MoS_2.

Figure 1.6 illustrates the synthesis and recovery cycles involved with an HDS catalyst. The production of this catalyst begins with the extraction of the components from the natural ores. Molybdenum occurs naturally as MoS_2, the mineral molybdenite. Cobalt sulfides and arsenides ($CoAs_2$, CoAsS, and Co_3S_4) are the compounds most frequently found in cobalt-containing ores, which usually also contain nickel, copper, and lead. The aluminum ore, bauxite, occurs as a mixture of aluminum hydroxide and aluminum oxide hydroxide, the fraction of each depending on the location. The ores are processed and refined to extract the purified elements in some usable form *(4)*.

The synthesis and processing of the working HDS catalyst involves slurrying the high surface area (finely divided) alumina support with solutions of molybdenum and cobalt, followed by firing to yield a mixture of the oxides ($CoO–MoO_3–Al_2O_3$) *(5)*. This oxidic form of the catalyst is then converted to the catalytically active sulfidic form during the HDS process, as it extracts sulfur from the petroleum feedstocks. After some time, the HDS activity of the catalyst drops, as a result of poisoning of the surface by deposits of carbonaceous material and by metals such as vanadium and nickel that are also extracted from the feedstock. The catalyst can be partially regenerated by burning off the carbonaceous material. However, the regeneration step does not remove the deposited metals, and eventually the activity can no longer be restored.

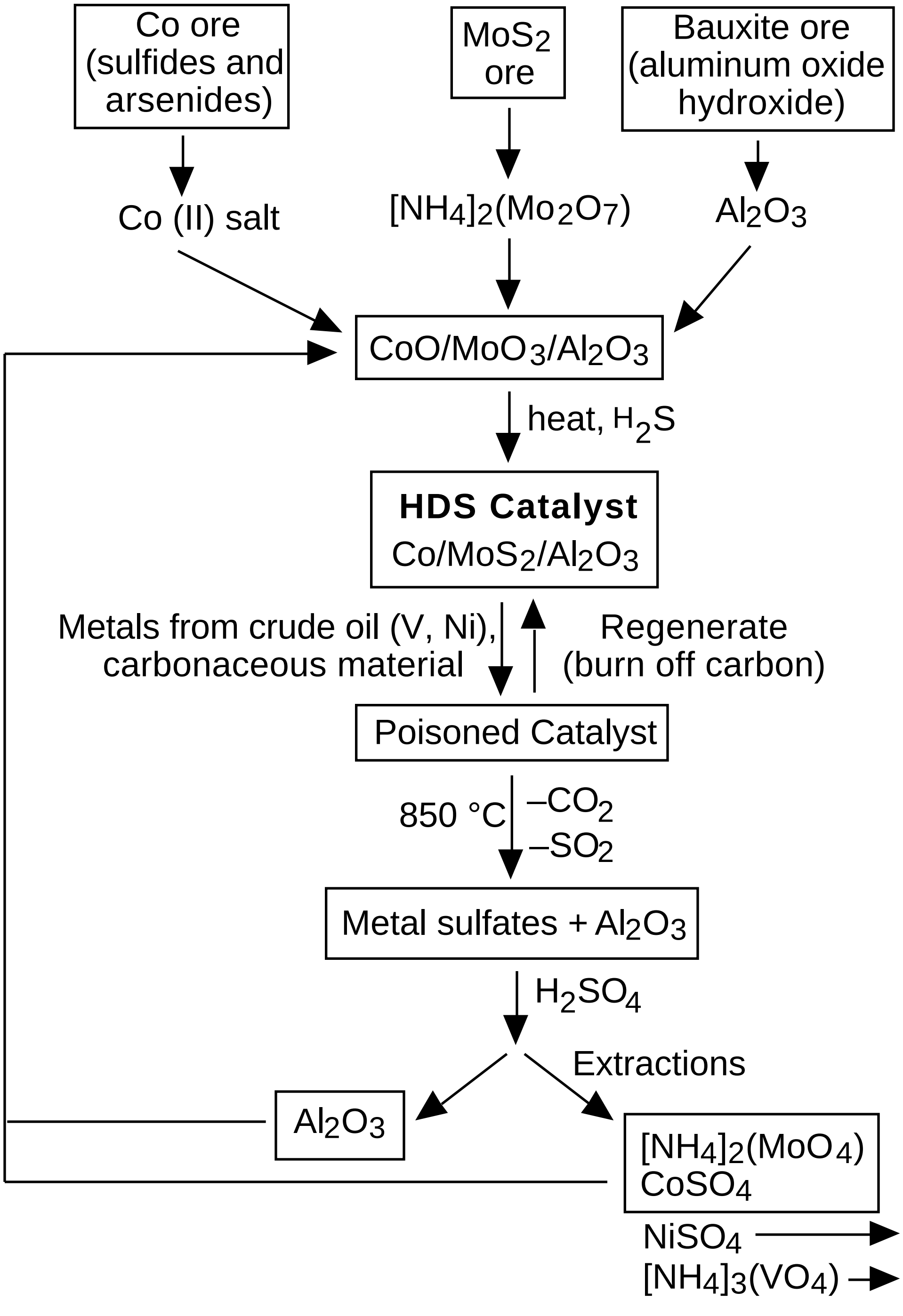

Figure 1.6. The life cycle of the components of a hydrodesulfurization catalyst.

In years past, the spent catalysts were committed to landfills; however, environmental concerns resulted in a ban on this practice in the mid-1980s. Recently, Metrex opened a plant in Heerlen, the Netherlands, that recovers the metals from spent HDS catalysts *(6)*. In the recycling process, the spent catalysts are first subjected to a heat treatment at 850 °C to remove the hydrocarbons and sulfur as CO_2 and SO_2 and to convert the metal sulfides to metal sulfates. The alumina support is recovered by leaching the catalyst in sulfuric acid, which dissolves the metal sulfates and leaves the alumina behind. By using a series of extractions, the individual metals can be separated and recovered as cobalt and nickel sulfates, ammonium vanadate, and ammonium molybdate. With this process, Metrex estimates a metals recovery efficiency greater than 90%. The metals and alumina are sold to companies that can use them, often in the preparation of additional batches of HDS catalysts.

The Age of Materials

Probably the best way to develop a feel for the vitality of the materials chemistry enterprise is with a few examples of current high-profile research activities and with materials and devices that already affect everyday life. Subsequent chapters of this book address many of the concepts underpinning these themes and amplify some of the examples given. Summaries of research opportunities in materials chemistry also were published recently *(3)*.

Analytical Methods: Thinking Small

The scanning tunneling microscope (STM) is an instrument that is revolutionizing the ability to image and manipulate matter. The principles underlying this instrument are given in Chapter 2. Researchers have already succeeded in imaging individual surface atoms on common metals (Figure 1.7) and semiconductors, whose physical structures are discussed in Chapters 3 and 5 and whose electronic structures are discussed in Chapter 7; in moving adsorbed atoms and molecules to desired locations on the surfaces of such substrates; and in fashioning “nanoelectrodes” and “nanobatteries,” representing electrochemistry on an unprecedentedly small scale (Figure 2.8).

Use of the atom-sized tip of the STM instrument as a kind of “atomic hole puncher” to carry out atomic-scale lithography is under development, as is the creation and characterization of wires that are one atom thick! An understanding of the effects of physical structure that control many of these applications is developed in Chapter 6.

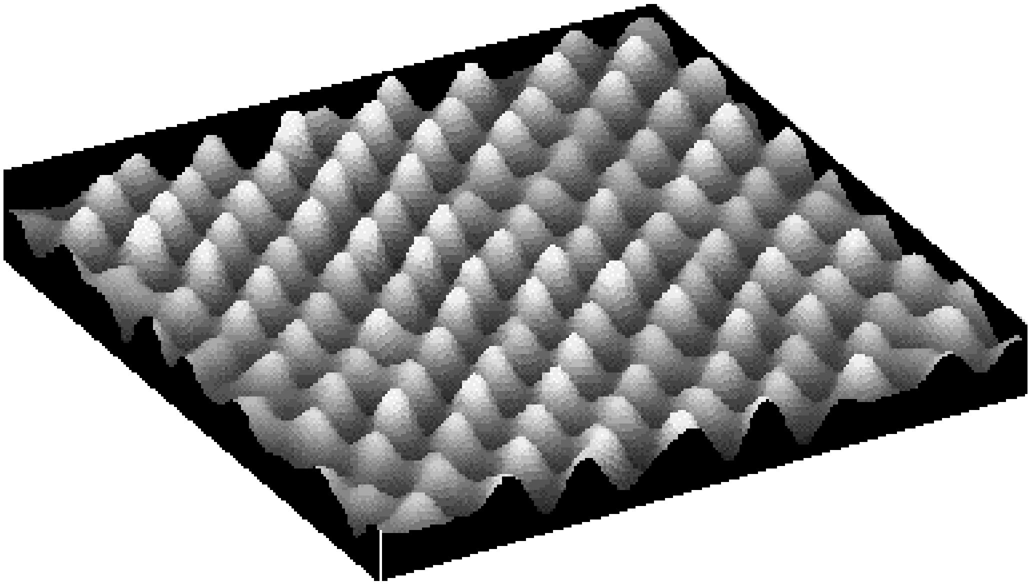

Figure 1.7. An STM-generated image of the surface of a gold crystal. (Original image courtesy of Burleigh Instruments, *see* Supplier Information.)

The pH sensor is another example of an analytical tool amenable to miniaturization. By placing dyes whose fluorescence is pH-dependent on the tips of optical fibers that are as small as 100 nm, the pH inside single biological cells and their substructures can be measured: The dyes can be excited by light-emitting diodes (LEDs) or diode lasers whose emitted light travels down the optical fibers; and the light emitted by the dye can be analyzed to determine the pH value of the medium in which it is immersed. Principles by which these semiconductor-based light sources and optical fibers operate are outlined in Chapters 8 and 10.

Machines represent a third rapidly moving area of analytical miniaturization, one that is heavily dependent on materials chemistry. Micromachines such as micromotors that are the size of a human hair have been prepared using polymer photoresists (for micrometer-scale patterning) and metal electroplating techniques. These machines are being proposed for use as on-line sensors in, for example, human bloodstreams, and as miniature gas chromatographs. Even smaller structures, nanostructures, are on the horizon.

Control of Interfaces

Interfaces, the zones where one material comes in contact with another, play a critical role in many devices based on electronic materials like semiconductors, metals, and superconductors. These solids, in which electrons are the mobile charge carriers, are discussed extensively in Chapters 5, 7, 8, and 9. The state of the art in growing certain solids like semiconductors is illustrated by the LEDs and diode lasers that have been mentioned in connection with pH sensing. As described in Chapter 10, techniques like chemical vapor deposition (CVD) can provide such exquisite control over the growth process that solids can be synthesized by depositing virtually an atomic layer at a time. This method permits the preparation of junctions that are essentially atomically abrupt. By controlling the chemical composition of these solids through the use of solid solutions, which are described in Chapter 3, such properties as the frequency of the light emitted by diodes may be tuned continuously over substantial regions of the visible and near-infrared spectrum.

Coatings and thin films play critical roles in the control of interfaces. An example of a coating with enormous potential is diamond. As discussed in Chapters 2, 5, and 7, diamond has a variety of remarkable properties, including exceptional hardness, high thermal conductivity, low electrical conductivity, chemical inertness, and optical transparency, that make it an ideal material for many industrial applications. Chapter 10 highlights some new, more cost-effective synthetic and processing routes to diamond films that have been discovered, and promise to extend the range of applications. Diamond films can serve to harden ceramic cutting tools, improve the scratch resistance of lenses in glasses, and enhance the quality of tweeters in loud speakers, to cite a few examples.

New Materials

The re-entrant foam alluded to earlier in the chapter illustrates the notion that we are at a stage where we can often design materials to have desired properties. Ferrofluids, discussed in Chapter 2, are another such example: suspensions of Fe_3O_4 magnetite particles that are roughly 100 Å in size elegantly provide magnetic control over the liquid ambient in which they are suspended through the cooperative interactions of electrons in the solid. This design feature is used to advantage in making rotating seals for high-vacuum equipment, for example.

High-temperature superconductors, which burst upon the scene in the late 1980s, have provided the impetus for preparing, characterizing, and modeling many new perovskite structures, which are described in Chapter 5. Important practical aspects of superconductivity—the unusually high temperatures at which the new ceramic materials lose their electrical resistance and expel magnetic fields from their interiors; the kinds of electrical current densities and magnetic field strengths they can withstand before reverting to nonsuperconducting electromagnetic properties; and strategies for fabricating them into useful shapes like thin films and wires for devices—provide a backdrop for this exciting research area and are covered in Chapter 9. Synthetic routes to these materials, compounds like $YBa_2Cu_3O_7$, are discussed in Chapter 10. Their variable stoichiometry is presented in Chapters 3 and 5.

Like high-temperature superconductors, fullerene-derived materials have had an enormous impact on the materials chemistry community in the short time they have been available for study. Isolated from soot that is generated from graphite electrodes, the parent soccer-ball-shaped C_{60}

compound, buckminsterfullerene, and its derivatives are being proposed as lubricants, organic magnets, frequency doubling materials, and substrates for the growth of diamond films. Samples of C_{60} have been reacted with several alkali metals to make relatively high-temperature superconductors of formula M_3C_{60} that are discussed in Chapters 5 and 9; the alkali metals occupy holes formed by octahedral and tetrahedral arrangements of close-packed C_{60} molecules in the solid state.

"Smart" Materials

An alloy of nickel and titanium exhibits several astonishing properties, described in Chapter 9, which identify it as a "smart" material capable of responding to external stimuli. For example, wires of NiTi "memory metal" can be bent at room temperature and, when gently warmed by a hair blower or hot water, will return to their original linear shape. Or the wire can be heated in a candle flame to give the sample a new shape that it will remember, a consequence of moving defects in the solid, which are discussed in Chapter 6. The solid-state phase change that accounts for these seemingly improbable transformations can also be initiated mechanically, an effect exploited in the manufacturing of eyeglass frames from NiTi that remember their shape. The ability to respond to mechanical and thermal stimuli is being used to create new kinds of actuators and sensors.

Chapter 2 presents electrorheological (ER) fluids as another example of "smart" materials. Ingredients as common as corn oil and flour can be used to prepare a suspension whose viscosity changes markedly with a strong applied electric field. Application of the electric field causes dipoles associated with the suspended particles to align and thereby creates a fibrous structure in the fluid that stiffens it. Automobile manufacturers are interested in such fluids as a means of damping vibrations that might otherwise damage the vehicle's engine block.

Optical fibers and diode light sources, discussed in Chapters 8 and 10, can help to identify structural flaws that might be developing in a material. For example, a network of these fibers, embedded in a structural feature like a concrete beam or aircraft wing, might be used to sense a developing fracture as a deviation in the light beam that is passing through the optical fiber network. Early detection of the fracture would permit the damaged component to be replaced before a catastrophic failure occurs.

Some of What's Already Here

High-tech materials and advanced devices already play a prominent role in everyday life. For example, the LEDs mentioned earlier serve as indicator lights for myriad appliances; and diode lasers are a key component of compact disk (CD) players.

Piezoelectric materials are also widely used. These crystals have the property that when an electric field is applied to them, they mechanically deform; and, conversely, when they are mechanically deformed, they generate an electric field. Variations in electric-charge distribution within such solids are discussed in Chapter 2. Examples of piezoelectric materials are quartz and so-called PZT ceramics, a group of perovskites, described in Chapter 5, that includes $PbZrO_3$ and $PbTiO_3$. These materials are used in a variety of devices, including loudspeakers, buzzers, electrical relays, and pressure gauges. Some torches are ignited by a spark that is produced by the electric field that results when a piezoelectric crystal is squeezed.

Our information technologies are heavily materials-dependent. For example, magnetic domains, which are discussed in Chapter 2, are used extensively in storage media such as floppy disks, magnetic tape, and hard drives for computers.

In medicine, a processing technique called thermal spraying has proven to be useful. Thermal spraying is a generic term for a variety of processes that heat, melt, and spray metallic, ceramic, carbide, or plastic particles onto a surface. The particles flatten upon impact and bond to the substrate. In order for tissue to adhere properly to an implant such as a stainless steel hip replacement, a coating must cover the implant. Hydroxyapatite, $Ca_5(PO_4)_3OH$, a mineral that is a component of teeth and bones, is applied to such implants in a plasma spray process and provides a bioceramic that promotes good tissue adhesion.

The detection of harmful radiation has benefited from developments in materials chemistry. Some polymers are being used as inexpensive detectors for alpha particles emitted by radon gas, because of defects created in the polymer structure by the alpha particles: more rapid chemical etching occurs at the defect sites and permits them to be identified and used as a measure of radon concentration, as discussed in Chapter 6 and Experiment 6.

Our air quality has been aided by the catalytic converter, which has been used to control automobile emissions since 1975, and will be applied to other internal combustion systems in the near future. These devices use metals such as platinum, palladium, and rhodium to catalyze the complete conversion of unburned hydrocarbons and to decrease the emission of nitrogen oxides. The catalyzed reactions occur at the surface of the metal particles that are dispersed onto ceramic (metal oxide) substrates that have highly porous honeycomb ceramic monoliths (Figure 1.8).

Thin film technologies have been used to make new kinds of jewelry and sunglasses from metal oxides. Titanium oxides are being used to create brightly colored, highly reflective earrings, for example; and metal oxides are used to make highly reflective coatings for “one-way” sunglasses. The high reflectivity of metals is discussed in Chapter 7.

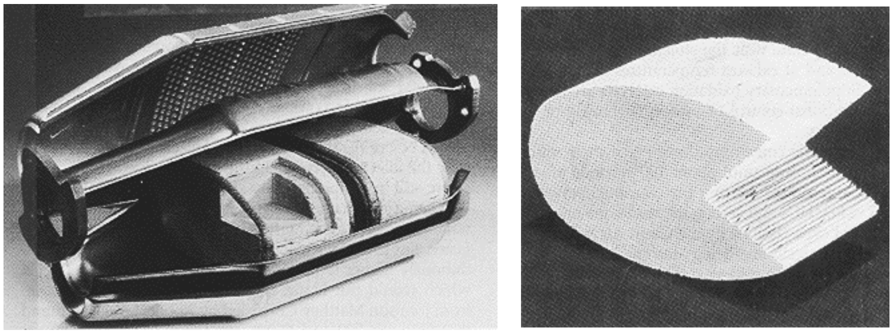

Figure 1.8. Cutaway view of Allied-Signal automotive catalytic converter (left) shows the interior of ceramic honeycomb monolith. The honeycomb (enlarged, right) contains 300 to 400 square channels per square inch, each coated with a porous, high-surface-area layer, such as activated alumina, on which precious metal catalysts are dispersed. Carbon monoxide and hydrocarbons in exhaust gases, which must pass through the channels, are catalytically converted to carbon dioxide and water. (Reproduced from reference 6. Copyright 1992 American Chemical Society.)

Finally, a popular product that is marketed in toy stores is Magic Sand. Control of the surface chemistry of sand particles by coating them with organosilanes causes them not to wet when placed in water. This effect is similar to that observed when fabric is sprayed with a silicone-based water repellent and provides another illustration of the importance of interfaces *(7)*.

In short, the Age of Materials presents extraordinary opportunities and challenges. The intent of the remainder of this volume is to make materials chemistry accessible to teachers and students by connecting solids to fundamental chemical and physical principles.

References

1. *Materials Science and Engineering for the 1990s: Maintaining Competitiveness in the Age of Materials*; National Research Council, National Academy Press: Washington, DC, 1989.
2. Lakes, R. *Science (Washington, DC)* **1987**, 235, 1038–1040.
3. *Advanced Materials and Processing: The Federal Program in Materials Science and Technology*; Committee on Industry and Technology/COMAT, National Institute for Standards and Technology: Gaithersburg, MD.
4. Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press: New York, 1984.
5. Furimsky, E. *Catal. Rev.-Sci. Eng.* **1980**, 22, 371.
6. O'Sullivan, D. *Chem. Eng. News* October 26, 1992, p 20.
7. Vitz, E. *J. Chem. Educ.* **1990**, *67*, 512.

Additional Reading

- Advanced Materials and Processing: The Federal Program in Materials Science and Technology; *A Report by the FCCSET Committee on Industry and Technology; Office of Science and Technology Policy. To Supplement the President's 1993 Budget. (Available from Committee on Industry and Technology/COMAT; Room B309, Materials Building; Gaithersburg, MD 20899; phone (301) 975–5655.)*
- Critical Technologies: The Role of Chemistry and Chemical Engineering; *A Report by the Board on Chemical Sciences and Technology; National Academy Press: Washington, DC, 1992. (Available from Board on Chemical Sciences and Technology; National Research Council; 2101 Constitution Ave, N.W. ; Washington, DC 20418.)*
- Materials Science and Engineering for the 1990s: Maintaining Competitiveness in the Age of Materials; *National Research Council, National Academy Press: Washington, DC, 1989.*
- *Drexler, K. E.* Nanosystems: Molecular Machinery, Manufacturing, and Computation*; Wiley: New York, 1992.*
- MRS Bulletin*, issued monthly by the Materials Research Society, Pittsburgh, PA.*

Exercises

1. To which corner or corners of the materials tetrahedron (Figure 1.1) can the following be assigned?
   a. The reaction used to prepare polyurethane foam.
   b. The mechanical properties of a sample of polyurethane foam.
   c. The temperature below which a material becomes a superconductor (its critical temperature).
   d. Conversion of C_{60} to K_3C_{60}.

2. Sketch a figure, similar to the one shown in Figure 1.3, that you think might illustrate the behavior of the pores in an untreated polyurethane foam as it is stretched.

3. If re-entrant foam is compressed instead of stretched, what do you predict will happen to the size of its cross-section? Explain your answer in terms of the idealized cubic re-entrant pore, Figure 1.3.

4. How might re-entrant foam be used? What advantages does it offer if it is to be inserted into a hole as a kind of fastener?

5. Investigate the life cycle of a material of interest to you: how the raw materials are obtained; the processing needed to make the material; the use(s) of the material; how the material is disposed of; its recyclability; its environmental impact; and the energy costs associated with the material. You have the option of researching your topic individually or in small groups over a period of several weeks. Optional: Present your results at a poster session in which you share what you have learned.