2

Some History

CHAPTER PREVIEW

In this chapter we present a brief history of ceramics and glasses. Because of the length of time over which they have been important to human existence it would be possible, indeed it has been done, to fill entire volumes on this one topic. We do not have the luxury of spending so much time on any one topic but history is important. In ceramics, it helps if we understand why certain events/developments occurred and when and how they did. We are really interested in setting the scene for many of the subsequent chapters. The earliest ceramics that were used were flint and obsidian. These exhibit conchoidal fracture like many modern day ceramics, such as cubic zirconia and glasses. This property enabled very sharp edges to be formed, which were necessary for tools and weapons. During the latter period of the Stone Age (the Neolithic period) pottery became important. Clay is relatively abundant. When mixed with water, it can be shaped and then hardened by heating. We will describe the different types of pottery and how the ceramics industry developed in Europe. The Europeans were not responsible for many of the early inventions in pottery; they were mostly trying to copy Chinese and Near East ceramics. Europe's contribution was to industrialize the process. We are also going to describe some of the major innovations in ceramics that occurred during the twentieth century, such as the float glass process, bioceramics, and the discovery of high-temperature superconductivity. These developments are important in defining the present status of the field and also give some indications of areas in which future innovations may occur. We will conclude the chapter by giving information about museums that have major collections of ceramic materials as well as listing the relevant professional societies.

2.1 EARLIEST CERAMICS: THE STONE AGE

Certain ancient periods of history are named after the material that was predominantly utilized at that time. The Stone Age, which began about 2.5 million years ago, is the earliest of these periods. Stone, more specifically flint, clearly satisfies our definition of a ceramic given in Chapter 1.

Flint is a variety of chert, which is itself cryptocrystalline quartz. Cryptocrystalline quartz is simply quartz (a polymorph of SiO_2) that consists of microscopic crystals. It is formed from silica that has been removed from silicate minerals by chemical weathering and carried by water as ultrafine particles in suspension. Eventually, it settles out as amorphous silica gel containing a large amount of water. Over time, the water is lost and small crystals form, even at low temperatures. During settling, the chemical conditions are changing slowly. As they change, the color, rate of deposition, and texture of the precipitate can also change. As a result, cryptocrystalline quartz occurs in many varieties, which are named based on their color, opacity, banding, and other visible features. Flint is a black variety of chert. Jasper is a red/brown variety.

Flint is easily chipped and the fracture of flint is conchoidal (shell-like), so that sharp edges are formed. The earliest stone tools are remarkably simple, almost unrecognizable unless they are found together in groups or with other objects. They were made by a process called percussion flaking, which results in a piece (a flake) being removed from the parent cobble (a core) by the blow from another stone (a hammer-stone) or hard object. Both the flake and the core have fresh surfaces with sharp edges and can be used for cutting. While pebble tools do have a cutting edge, they are extremely simple and unwieldy. These basic tools changed, evolved, and improved through time as early hominids began to remove more flakes from the core, completely reshaping it and creating longer, straighter cutting edges. When a core assumes a distinctive teardrop shape, it is known as a handaxe, the hallmark of *Homo erectus* and early *Homo sapiens* technology. Figure 2.1 shows an example of a stone tool made by percussion flaking that was found in Washington State.

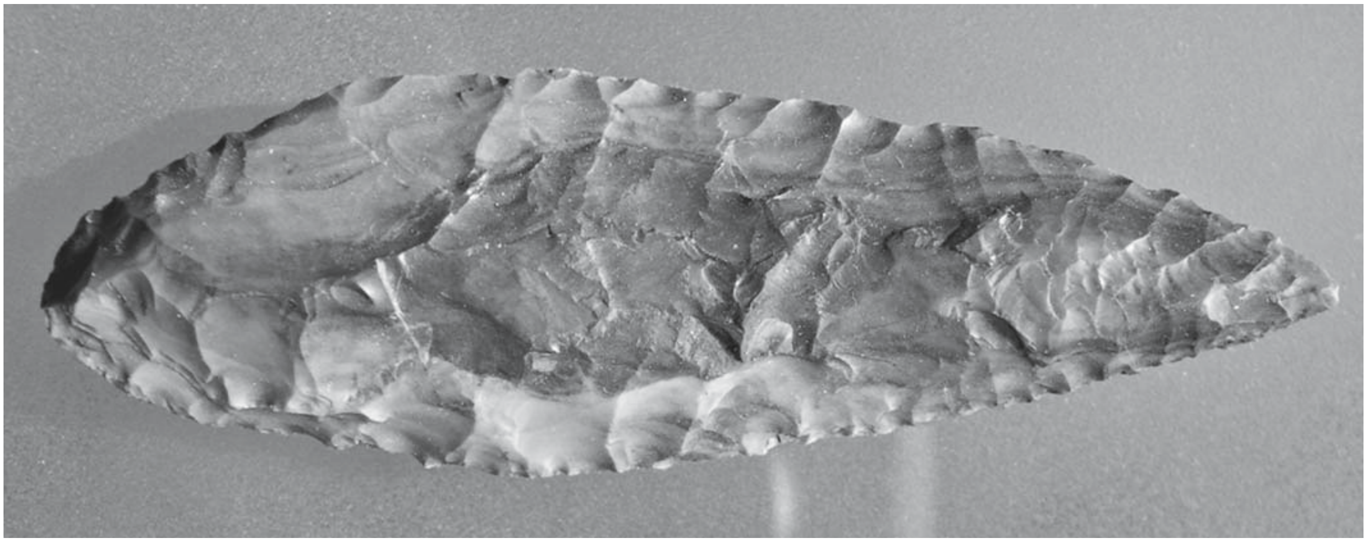

FIGURE 2.1 Example of a stone tool made by percussion flaking.

Period	Years Before Present	Stone Industry	Archaeological Sites	Hominid Species	Major Events
Neolithic	10,000				Farming
Upper Paleolithic		Blade tools	Lascaux Pincevent Dolni Vestonice		Art
			Tabun	*Homo sapiens sapiens*	
Middle Paleolithic		Mousterian flake tools	Shanidar Klasies River	*Homo sapiens neanderthalensis*	
Lower Paleolithic	100,000		Verteszöllös Kalambo Falls	Archaic *Homo sapiens*	Burial of dead
	200,000		Torraiba		Oldest dwellings
			Terra Amata Olorgesailie		Use of fire
	500,000		Zhoukoudien Trinil		Spread out of Africa
		Clactonian chopping tools			
	1,000,000				Handaxes
		Acheulean handaxes		*Homo erectus*	
Basal Paleolithic	2,000,000	Oldowan pebble tools	Koobi Fora Olduvai Swartkrans	*Homo habilis*	Large brains First stone tools
	3,000,000		Hadar Laetoli	*Australopithecus*	
	6,000,000			*Ardipithecus*	Oldest hominid fossils

FIGURE 2.2 Chronology of the Stone Age.

Christian Thomsen first proposed the division of the ages of prehistory into the Stone Age, Bronze Age, and Iron Age for the organization of exhibits in the National Museum of Denmark in 1836. These basic divisions are still used in Europe, the United States, and in many other areas of the world. In 1865 English naturalist John Lubbock further divided the Stone Age. He coined the terms Paleolithic for the Old Stone Age and Neolithic the New Stone Age. Tools of flaked flint characterize the Paleolithic period, while the Neolithic period is represented by polished stone tools and pottery. Because of the age and complexity of the Paleolithic, further divisions were needed. In 1872, the French prehistorian Gabriel de Mortillet proposed subdividing the Paleolithic into Lower, Middle, and Upper. Since then, an even earlier subdivision of the Paleolithic has been designated with the discovery of the earliest stone artifacts in Africa. The Basal Paleolithic includes the period from around 2.5 million years ago until the appearance and spread of handaxes. These different periods are compared in Figure 2.2.

Stone tools that were characteristic of a particular period are often named after archeological sites that typified a particular technological stage.

- Oldowan pebble tools were found in the lowest and oldest levels of Olduvai Gorge.
- Acheulean handaxes are named after the Paleolithic site of St. Acheul in France, which was discovered in the nineteenth century.
- Clactonian chopping tools are named after the British site of Clacton-on-sea, where there is also the earliest definitive evidence for wood technology in the prehistoric record—the wood was shaped using flint tools.
- Mousterian flake tools are named after a site in France. The later blade tools are flakes that are at least twice as long as they are wide.

Another important ceramic during the Stone Age was obsidian, a dark gray natural glass precipitated from volcanic lava. Like other glasses it exhibits conchoidal fracture and was used for tools and weapons back into the Paleolithic period.

2.2 CERAMICS IN ANCIENT CIVILIZATIONS

The oldest samples of baked clay include more than 10,000 fragments of statuettes found in 1920 near Dolní Vestonice, Moravia, in the Czech Republic. They portray wolves, horses, foxes, birds, cats, bears, or women. One of these prehistoric female figures, shown in Figure 2.3, remained almost undamaged. It was named the “Venus of Vestonice” and is believed to have been a fertility charm. The absence of facial features on this and other “Venus” figures is causing many anthropologists to rethink the role these figures might have played in prehistoric society. The statuette stands about 10 cm tall and has been dated as far back as 23,000 BCE. One of the most recent archeological finds was made in the caves of Tuc d’Audobert in France, where beautifully preserved clay bison have been found that are estimated to be 12,000 years old.

FIGURE 2.3 A 25,000-year old baked clay Pavlovian figurine called the “Venus of Vestonice”; found in 1920 in Dolni Vestonice in the Czech Republic.

The earliest archeological evidence of pottery production dates back to about 10,000 BCE and the discovery of fragments from a cave dwelling near Nagasaki, Japan. This type of pottery is called Jomon pottery because of the characteristic surface patterns, which were made with a twisted cord. Jomon means “cord pattern.” The pottery also featured patterns made with sticks, bones, or fingernails. These vessels, like those produced in the Near East about 10,000 years ago, were fired at a low temperature compared to modern day pottery production.

By 6400 BCE, pottery making was a well-developed craft. Subsequent developments in the history of ceramics are shown in Figure 2.4. We will be describing some of these in a little more detail in later sections of this chapter.

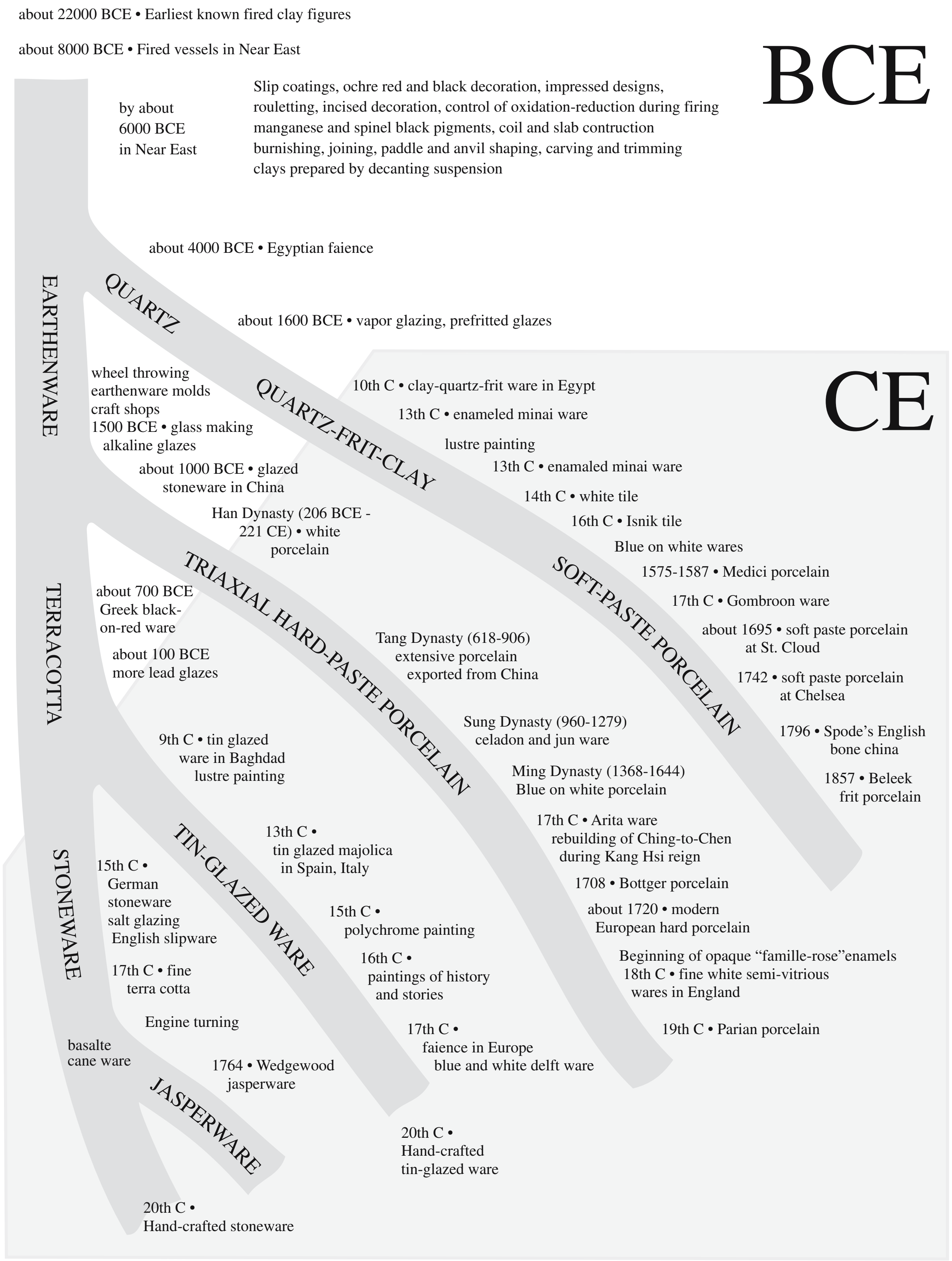

FIGURE 2.4 The "flow" of ceramic history illustrates the mainstreams of earthenware, terra cotta, and stoneware, of "triaxial" hard-paste porcelain, of quartz-based bodies, and of tin-glazed ware. Some important shaping and decorative techniques are illustrated, but the diagram is far from complete.

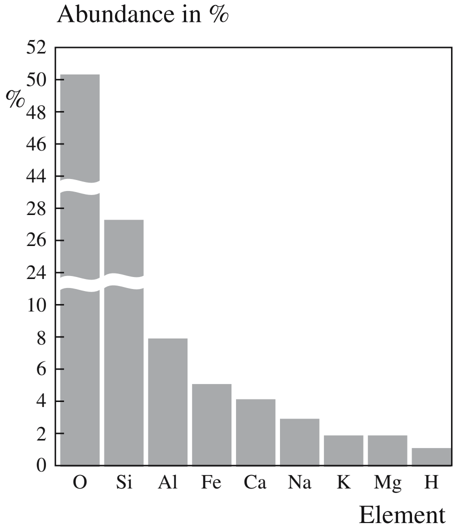

FIGURE 2.5 Abundance of common elements in the earth's crust.

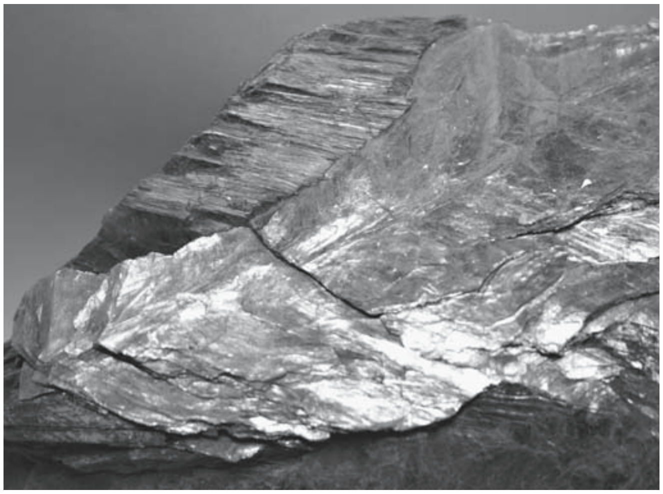

FIGURE 2.6 Large "grains" of mica clearly show the lamellar nature of the mineral. Two orientations are present in this one piece.

2.3 CLAY

Silicate minerals make up the vast majority of the earth's crust, which is not surprising if we consider

- The abundance of Si and O (Figure 2.5)
- The high strength of the Si–O bond (Table 2.1)

Since silicate and aluminum silicate minerals are widely available, they are inexpensive and form the backbone of the traditional high-volume products of the ceramic industry. Their abundance also explains why earthenware products are found in nearly every part of the world. The situation is very different with regard to kaolinite, the essential ingredient, along with feldspar and quartz, needed to make porcelain, by far the finest and most highly prized form of ceramic. Kaolin deposits are more localized. There are excellent deposits, for example, in southwest England. In the United States most kaolin comes from the southeast between central Georgia and the Savannah River area of South Carolina.

Clay minerals remain the most widely used raw materials for producing traditional ceramic products. The total U.S. production of clays is about 40 million tons per year, valued at $1.5 billion.

TABLE 2.1 Bond Strengths with Oxygen

Bond	*Strength (kJ/mol)*
Ti-O	674
Al-O	582
Si-O	464
Ca-O	423
Mn[a]-O	389
Fe[a]-O	389
Mg-O	377

[a] 2+ state.

The clay minerals are layered or sheet silicates with a grain size <2 μm. Chemically they are aluminosilicates. In nature, mica (shown in Figure 2.6) is constructed by stacking layers together to form sheets. Kaolinite has a related structure but tends to have smaller "grains." Rocks that contain a large amount of kaolinite are known as kaolin. When the sheets are separated by films of water, the platelets slide over one another to add plasticity to the mixture. This plasticity is the basis of the use of clay for pottery. Moreover, when the clay–water mixture is dried it becomes hard and brittle and retains its shape. On firing at temperatures about 950°C, the clay body becomes dense and strong. In Chapter 7 we describe the structures of some of the important clay minerals, including kaolin.

2.4 TYPES OF POTTERY

Pottery is broadly divided into

- Vitrified ware
- Nonvitrified ware

The classification depends upon whether the clay was melted during the firing process into a glassy (vitreous) substance or not. Within these divisions we have the following:

- *Earthenware* is made from red "earthenware clay" and is fired at fairly low temperatures, typically between 950 and 1050°C. It is porous when not glazed, relatively coarse, and red or buffcolored, even black after firing. The term "pottery" is often used to signify earthenware. The major earthenware products are bricks, tiles, and terra cotta vessels. Earthenware dating back to between 7000 and 8000 BCE has been found, for example, in Catal Hüyük in Anatolia (today's Turkey).

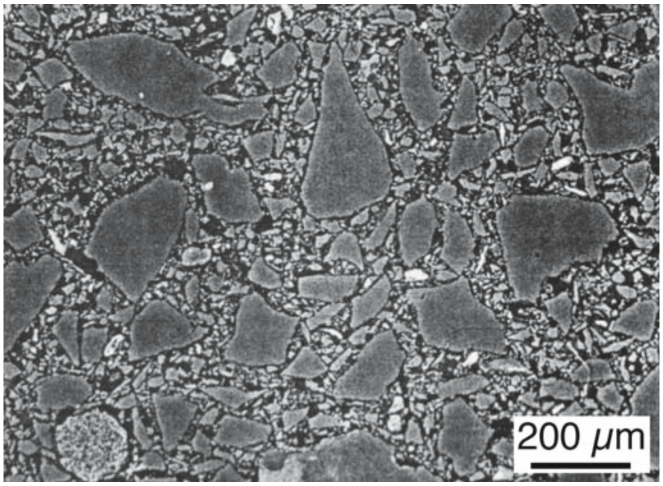

FIGURE 2.7 Microstructure of a “Masters of Tabriz” tile showing many large grains of crystalline SiO_2.

- *Stoneware* is similar to earthenware but is fired to a higher temperature (around 1200–1300°C). It is vitrified, or at least partially vitrified, and so it is nonporous and stronger. Traditional stoneware was gray or buff colored. But the color can vary from black via red, brown, and gray to white. Fine white stoneware was made in China as early as 1400 BCE (Shang dynasty). Johann Friedrich Böttger and E.W. von Tschirnhaus produced the first European stoneware in Germany in 1707. This was red stoneware. Later Josiah Wedgwood, an Englishman, produced black stoneware called basalte and white stoneware colored by metal oxides called jasper.
- *Porcelain* was invented by the Chinese and produced during the T’ang dynasty (618–907 CE). It is a white, thin, and translucent ceramic that possesses a metal-like ringing sound when tapped. Porcelain is made from kaolin (also known as china clay), quartz, and feldspar. Fired at 1250–1300°C it is an example of vitreous ware. The microstructure of porcelain is quite complicated. Figure 2.7 shows a backscattered electron image obtained using a scanning electron microscope (SEM) of the microstructure of a “Masters of Tabriz” tile (1436 CE) showing that it contains many large grains of quartz immersed in a continuous glass phase.
- *Soft-paste porcelain* is porcelain with low clay content that results in a low alumina (Al_2O_3) content. The most common form of soft-paste porcelain is formed of a paste of white clay and ground glass. This formulation allows a lower firing temperature, but provides a less plastic body. Not being very tough, it is easily scratched and more rare than hard-paste porcelain.
- *Hard-paste porcelain* is porcelain with a relatively high alumina content derived from the clay and feldspar, which permits good plasticity and formability, but requires a high firing temperature (1300–1400°C). Böttger produced the first successful European hard-paste porcelain in 1707–1708 consisting of a mixture of clay and gypsum. This work laid the foundation for the Meissen porcelain manufacture in Saxony (Germany) in 1710.
- *Bone China* has a similar recipe to hard-paste porcelain, but with the addition of 50% animal bone ash (calcium phosphate). This formulation improves strength, translucency, and whiteness of the product and was perfected by Josiah Spode at the end of the eighteenth century. It was then known as “English China” or “Spode China.”

2.5 GLAZES

To hermetically seal the pores of goods made of earthenware an additional processing step called glazing was introduced around or probably even before 3000 BCE by the Egyptians. It involved the coating of the fired objects with an aqueous suspension consisting of finely ground quartz sand mixed with sodium salts (carbonate, bicarbonate, sulfate, chloride) or plant ash. The ware would then be refired, usually at a lower temperature, during which the particles would fuse into a glassy layer.

Two other types of glaze, which also date back several millennia, have been applied to earthenware. These are the transparent lead glaze and the opaque white tin glaze.

The Lead Glaze

The addition of lead reduces the melting or fusion point of the glaze mixture, which allows the second firing to be at an even lower temperature. The first lead-rich glazes were probably introduced during the Warring States period (475–221 BCE). The lead oxide (PbO) content was about 20%. During the Han dynasty (206 BCE–CE 200) higher lead oxide contents were typical, up to 50–60%. Lead glazing was subsequently widely used by many civilizations. However, lead from the glaze on tableware may be leached by food. Table 2.2 shows lead released from two glazes that were made to match those of two Eastern Han Dynasty lead glazes. The glaze formulations were remade

TABLE 2.2 Composition of Han Lead Glazes (wt%) and Lead Metal Release (ppm)

	PbO	*SiO_2*	*Al_2O_3*	*Fe_2O_3*	*TiO_2*	*CaO*	*MgO*	*K_2O*	*Na_2O*	*BaO*	*CuO*	*SnO_2*	*Cl*	*S*	*Pb release*
Glaze 1	59.7	29.5	3.7	1.3	0.2	1.9	0.5	0.9	0.2	0.2	1.2	0.2	2.2	—	42
Glaze 2	43.5	33.4	3.9	2.0	0.6	2.0	0.7	0.5	0.4	7.7	3.0	1.2	—	0.6	120

and fired by CERAM (formerly the British Ceramic Research Association) in the UK. The amount of lead released in a standard leach test is determined by filling the glazed ceramic item with 4% acetic acid at 20°C for 24 hours; the acid is then analyzed for Pb by flame atomic absorption spectrometry. The present U.S. Food and Drug Administration limit for Pb release from small hollowware is 2 ppm.

Some historians believe that lead release from glazes on pitchers and other food and beverage containers and utensils poisoned a large number of Roman nobility and thus contributed (together with Pb from water pipes) to the fall of the Roman Empire (see, for example, Lindsay, 1968). Lead poisoning was responsible for the high mortality rates in the pottery industry even during the nineteenth century. Many countries have now outlawed lead glazing unless fritted (premelted and powdered) glazes are utilized that prevent the lead from being easily leached. The possibility of leaching a heavy metal from a glass is a concern today in the nuclear-waste storage industry.

The Tin Glaze

The Assyrians who lived in Mesopotamia (today's Northern Iraq) probably discovered tin glazing during the second millennium BCE. It was utilized for decorating bricks, but eventually fell into disuse. It was reinvented again in the ninth century CE and spread into Europe via the Spanish island of Majorca, after which it was later named (*Majolica*). Centers of majolica manufacture developed in Faenza in Italy (*Faience*) and in 1584 at the famous production center at Delft in the Netherlands (*Delftware*). Tin glazing became industrially important at the end of the nineteenth century with the growth of the ceramic sanitary ware industry.

2.6 DEVELOPMENT OF A CERAMICS INDUSTRY

Quantity production of ceramics began during the fourth millennium BCE in the Near East. Transition to a large-scale manufacturing industry occurred in Europe during the eighteenth century. At the beginning of the century, potteries were a craft institution. But this situation was transformed at several important sites:

- Vincennes and Sèvres in France
- Meißen in Germany
- Staffordshire in England

By the end of the eighteenth century, the impact of greater scientific understanding (such as chemical analysis of raw materials) had changed the field of ceramics. At the same time, the ceramic industry played an influential role in the industrial revolution and the development of factory systems in England and across Europe. Ceramics became an important and growing export industry that attracted entrepreneurs and engineers to develop modern production and marketing methods. A leader in this revolution was Josiah Wedgwood.

In 1767 Wedgwood produced improved unglazed black stoneware, which he called "basalte." The famous Wedgwood "jasperware" began production in 1775 and consisted of

- One part flint
- Six parts barium sulfate
- Three parts potters' clay
- One-quarter part gypsum

Wedgwood was so excited by this new ceramic body that he wrote to his partner:

> The only difficulty I have is the mode of procuring and conveying incog (*sic*) the raw material. . . . I must have some before I proceed, and I dare not have it in the nearest way nor undisguised.

Jasper is white but Wedgwood found that it could be colored an attractive blue by the addition of cobalt oxide. (The mechanism for color formation in transition metal oxides is described in Chapter 32.) The manufacturing process was soon changed (in part because of a sharp increase in the cost of the blue pigment) and the white jasper was coated with a layer of the colored jasper. Wedgwood jasper remains sought after and highly collectable. You can visit the Wedgwood factory in England and watch the production process.

Wedgwood also was instrumental in changing the way manufacturing was done. He divided the process into many separate parts, and allowed each worker to become expert in only one phase of production. This approach was revolutionary at the time and was designed to increase the performance of each worker in a particular area and reduce the requirement for overall skill. He was also concerned with trade secrets; each workshop at his factory had a separate entrance so workers would not be exposed to more than a limited number of valuable secrets.

In the increasingly competitive entrepreneurial economy of the eighteenth century, Wedgwood was one of the leading figures to have the foresight and the willingness to expend the necessary effort to promote the general interests of the ceramics industry. In the early days of the pottery industry in England, transport of raw materials in and product out was done with pack animals. It was clear that quantity production could not be achieved without better transportation. Wedgwood organized a potters' association to lobby for better roads and, more importantly, a canal system. The opening of the Trent-Mersey Canal in 1760 ensured that Staffordshire would remain the center of English pottery production.

As with many industries, the first stage of the industrial revolution did not result in a deterioration of working conditions. A partly rural craft-based skill, such as pottery making, became an injurious occupation only as industrialization progressed, bringing into overcrowded town centers poor workers from the countryside. Occupational diseases were prevalent in the potteries. The main problem was diagnosed at an early date—lead poisoning. In 1949 British regulations forbade the use of raw lead in glaze compositions. Prior to this there were 400 cases of lead poisoning a year at the end of the nineteenth century. Although experiments with leadless glazes were recorded throughout the nineteenth century, lead was essential, and the safe solution adopted and approved early in the twentieth century was a lead glaze of low solubility, produced by making the glaze suspension out of fritted lead.

Another serious health risk for potters was pneumoconiosis: flint dust particles when inhaled caused gradual and often fatal damage to the lungs. It was a lingering disease, which took many decades to diagnose and control. Flint is still used as a component in the bodies of many traditional ceramic wares, but the risk of pneumoconiosis has been virtually eliminated through proper ventilation, the cleanliness of workshops, and the use of protective clothing.

PORTLAND CEMENTS

Hydraulic materials—water causes setting and hardening.

In North America the origin of pottery production occurred in regions where there were deposits of earthenware clay and the wood needed for the kilns. The abundance of these raw materials were factors in the English settling in Jamestown, Virginia in 1607. And there is evidence that pottery production began in Jamestown around 1625 (see Guillard, 1971). Similar supplies were available in the Northeast for the English potters accompanying the small band of farmers and tradesmen who arrived in Plymouth in the 1620s. In New England and in Virginia potters used a lead glaze brushed onto the inside of the earthenware vessel to make the porous clay watertight. The important pottery centers in North America during the mid-nineteenth century were Bennington, VT, Trenton, NJ, and East Liverpool, OH. The geographical location of each center formed a right triangle located in the northeast. These locations had deposits of fine clay and river transportation, which provided easy access to markets. By 1840 there were more than 50 stoneware potteries in Ohio, earning Akron the tag "Stoneware City."

In the past, ceramic production was largely empirical. To maintain uniformity, producers always obtained their raw materials from the same supplier and avoided changing any detail of their process. The reason was that they were dealing with very complex systems that they did not understand. Today, as a result of ~100 years of ceramics research, processing and manufacturing are optimized based on an understanding of basic scientific and engineering principles. Research in ceramics was spurred on by two main factors:

- Development of advanced characterization techniques such as X-ray diffraction and electron microscopy, which provided structural and chemical information
- Developments in ceramic processing technology

2.7 PLASTER AND CEMENT

A special ceramic is hydraulic (or water-cured) cement. World production of hydraulic cement is about 1.5 billion tons per year. The top three producers are China, Japan, and the United States. When mixed with sand and gravel, we obtain concrete—the most widely utilized construction material in the industrialized nations. In essence, concrete is a ceramic matrix composite (CMC) in which not just the matrix but also the reinforcing material is ceramic.

Ancient Romans and Greeks, 2000 years ago, pioneered the use of cement. Its unique chemical and physical properties produced a material so lasting that it stands today in magnificent structures like the Pantheon in Rome. Roman cement consisted of a mixture of powdered lime (CaO) and volcanic ash (a mixture of mainly SiO_2, Al_2O_3, and iron oxide)—called *pozzolana*—from Mount Vesuvius, which buried the ancient city of Pompeii in 79 CE. This mixture hardens in the presence of water.

Contemporary hydraulic cement, for example, Portland cement (invented by Joseph Aspdin and named after a natural stone from the island of Portland in England, which it resembles), has a composition similar to pozzolanic cement. The chief ingredients of Portland cement are di- and tricalcium silicates and tricalcium aluminate. In the reduced nomenclature given in Table 2.3 these ingredients would be expressed as C_2S, C_3S, and C_3A, respectively. Portland cement is produced to have a specific surface area of ~300 m^2/kg and grains between 20 and 30 μm. The average composition is given in Table 2.4. In Chapter 8 we will show you on a ternary phase diagram the composition range of Portland cements.

The setting reactions for Portland cement are similar to those for the ancient pozzolanic cement. The first reaction is the hydration of C_3A. This reaction is rapid, occurring within the first 4 hours, and causes the cement to set:

$$C_3A + 6H \rightarrow C_3AH_6 + \text{heat} \qquad (2.1)$$

TABLE 2.3 Reduced Nomenclature for Cement Chemistry

Lime CaO = C
Alumina Al_2O_3 = A
Silica SiO_2 = S
Water H_2O = H

TABLE 2.4 Average Overall Composition of Portland Cement Clinker

By element	*wt%*	*By Phase*	*Reduced nomenclature*	*Name*	*wt%*
CaO	60–67	3CaO·SiO$_2$	C$_3$S	Tricalcium silicate	45–70
SiO$_2$	17–25	2CaO·SiO$_2$	C$_2$S	Dicalcium silicate	25–30
Al$_2$O$_3$	3–9	3CaO·Al$_2$O$_3$	C$_3$A	Tricalcium aluminate	5–12
Fe$_2$O$_3$	0.5–6	4CaO·Al$_2$O$_3$ Fe$_2$O$_3$	C$_4$AF	Tricalcium aluminoferrite	5–12
MgO	0.1–4	CaSO$_4$·2H$_2$O	CSH$_2$	Gypsum	3–5
Na$_2$O, K$_2$O	0.5–1.3				
SO$_3$	1–3				

The C_3AH_6 phase or ettringite is in the form of rods and fibers that interlock. The second reaction, which causes the cement to harden, is slower. It starts after about 10 hours, and takes more than 100 days to complete. The product is tobermorite gel, a hydrated calcium silicate ($Ca_3Si_2O_7 \cdot 3H_2O$), which bonds everything together.

$$2C_2S + 4H \rightarrow C_3S_2H_3 + CH + \text{heat} \qquad (2.2)$$

$$2C_3S + 6H \rightarrow C_3S_2H_3 + 3CH + \text{heat} \qquad (2.3)$$

Protuberances grow from the gel coating and form arrays of interpenetrating spines. Scanning electron microscopy (SEM) has been one tool that has been used to examine cement at various stages in the setting and hardening process. Figure 2.8 shows an SEM image recorded 8 days into the hardening process. The plate-like features are calcium hydroxide (CH); the cement (Ct) grains are already completely surrounded by the tobermorite gel (called CSH in Figure 2.8).

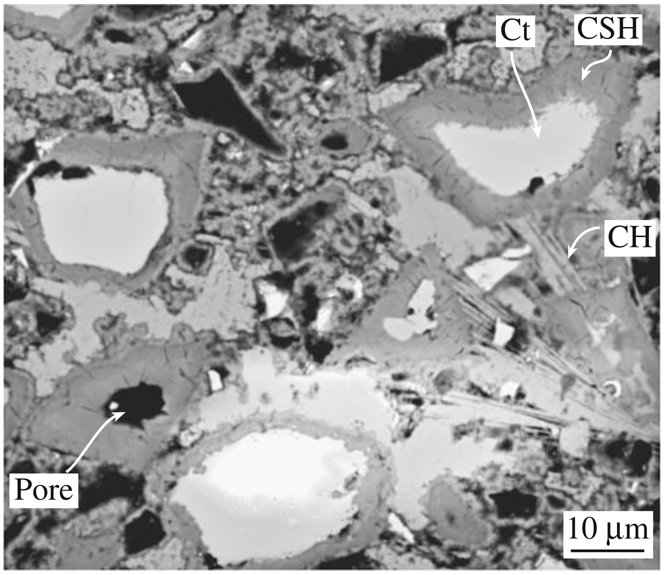

FIGURE 2.8 Reaction products in cement after 8 days hardening (SEM image).

The development of strength with time for Portland cement is shown in Figure 2.9. The reactions give off a lot of heat (Figure 2.10). In very large concrete structures, such as the Hoover Dam at the Nevada–Arizona border in the United States, heat is a potential problem. Cooling pipes must be embedded in the concrete to pump the heat out. These pipes are left in place as a sort of reinforcement. In the case of the Hoover Dam, the construction

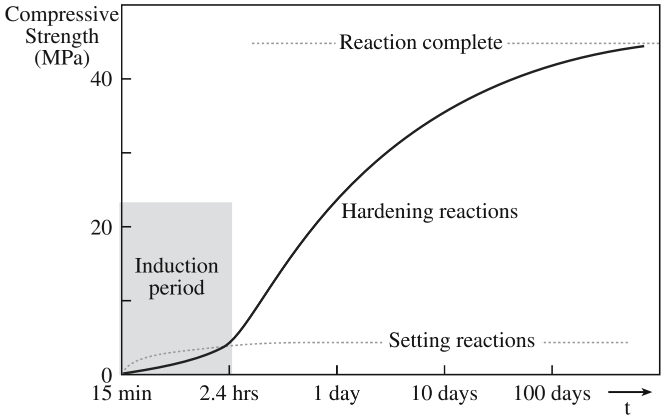

FIGURE 2.9 Increase in compressive strength of Portland cement with time.

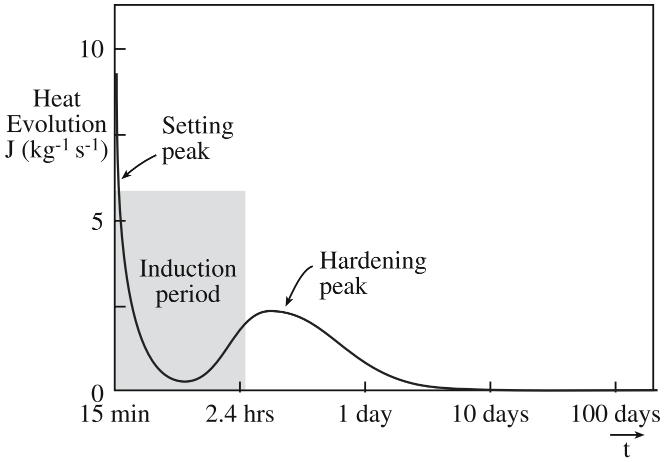

FIGURE 2.10 Heat evolution during the setting and hardening of Portland cement.

consisted of a series of individual concrete columns rather than a single block of concrete. It is estimated that if the dam were built in a single continuous pour, it would have taken 125 years to cool to ambient temperatures. The resulting stresses would have caused the dam to crack and possibly fail.

Plaster of Paris is a hydrated calcium sulfate ($2CaSO_4 \cdot H_2O$). It is made by heating naturally occurring gypsum ($CaSO_4 \cdot 2H_2O$) to drive off some of the water. When mixed with water, plaster of Paris sets within a few minutes by a cementation reaction involving the creation of interlocking crystals:

$$CaSO_4 \cdot \frac{1}{2}H_2O + \frac{3}{2}H_2O \rightarrow CaSO_4 \cdot 2H_2O \qquad (2.4)$$

To increase the setting time a retarding agent (the protein keratin) is added. Plaster of Paris is named after the French city where it was made and where there are abundant gypsum deposits. Following the Great Fire of London in 1666 the walls of all wooden houses in the city of Paris were covered with plaster to provide fire protection. The earliest use of plaster coatings dates back 9000 years and was found in Anatolia and Syria. The Egyptians used plaster made from dehydrated gypsum powder mixed with water as a joining compound in the magnificent pyramids.

2.8 BRIEF HISTORY OF GLASS

The history of glass dates back as far as the history of ceramics itself. We mentioned in Section 2.1 the use of obsidian during the Paleolithic period. It is not known for certain when the first glass objects were made. Around 3000 BCE, Egyptian glassmakers systematically began making pieces of jewelry and small vessels from glass; pieces of glass jewelry have been found on excavated Egyptian mummies. By about 1500 BCE Egyptian glassmakers during the reign of Touthmosis III had developed a technique to make the first usable hollowware.

The glass was made from readily available raw materials. In the clay tablet library of the Assyrian King Ashurbanipal (669–626 BCE) cuneiform texts give glass formulas. The oldest one calls for 60 parts sand, 180 parts ashes of sea plants, and 5 parts chalk. This recipe produces an Na_2O–CaO–SiO_2 glass. The ingredients are essentially the same as those used today but the proportions are somewhat different. Pliny the Elder (23–79 CE) described the composition and manufacture of glass in *Naturalis Historia*. During Roman times glass was a much-prized status symbol. High-quality glassware was valued as much as precious metals.

Figure 2.11 shows a Flemish drawing from the early fifteenth century depicting glass workers in Bohemia, from the *Travels of Sir John Mandeville*. It shows the legendary pit of Mynon with its inexhaustible supply of sand.

FIGURE 2.11 Glass workers in Bohemia, from the *Travels of Sir John Mandeville*, ink and tempera on parchment, Flemish, early fifteenth century.

> And beside Acre runs a little river, called the Belyon [Abellin], and near there there is the Fosse of Mynon, all round, roughly a hundred cubits broad; and it is full of gravel. And however much be taken out in a day, on the morrow it is as full as ever it was, and that is a great marvel. And there is always a great wind in that pit, which stirs up all the gravel and makes it eddy about. And if any metal be put therein, immediately it turns to glass. This gravel is shiny, and men make good clear glass of it. The glass that is made of this gravel, if it be put back in the gravel, turns back into gravel, as it was at first. And some say it is an outlet of the Gravelly Sea. People come from far countries by sea with ships and by land with carts to get some of that gravel.

Sand is an important constituent of most oxide glasses. Early glassmakers would have made effective use of natural resources and set up their workshops near a source of raw materials. This practice was also adopted during the time of Josiah Wedgwood and was the reason that the ceramic industry developed in the north of England—not in London, the capital. The illustration also shows the entire cycle of producing a glass object from obtaining the raw materials to testing of the final product.

One of the most common methods used to form glass is glassblowing. Although this technique was developed over 2000 years ago in Syria the glassblowing pipe has not changed much since then. The main developments are the automated processes used to produce glass containers and light bulbs in the thousands. In Chapter 21 we will summarize the important milestones in glass formation and production.

In this section we consider two specific aspects of the history of glass:

- Lead crystal glass
- Duty on glass

These events occurred between the very early experimentation with glass in Egyptian and other ancient civilizations and more modern developments in glass such as optical fibers and glass ceramics.

The Venetians used pyrolusite (a naturally occurring form of MnO_2) as a decolorizer to make a clear glass. This addition was essential because the presence of impurities, chiefly iron, in the raw materials caused the glass to have an undesirable greenish-brown color. The manganese oxidizes the iron, and is itself reduced. The reduced form of manganese is colorless but when oxidized it is purple (Mn in the +7 oxidation state). Manganese was used until quite recently as a decolorizer and some old windows may be seen, particularly in Belgium and the Netherlands, where a purple color has developed owing to long exposure to sunlight, which has oxidized the manganese back to the purple form.

Lead crystal glass is not crystalline. But the addition of large amounts of lead oxide to an aluminosilicate glass formulation produces a heavy glass with a high refractive index and excellent transparency. Suitable cutting, exploiting the relative ease with which lead glass can be cut and polished, enhances the brilliance. The lead content, in the form of PbO, in Ravenscroft's lead crystal glass has been determined to be about 15%. Now lead crystal glasses contain between 18 and 38% PbO. For tableware to be sold as "lead crystal" the PbO content must be about 25%.

Expansion of the British glass industry followed the success of lead crystal glass and during the eighteenth century it achieved a leading position that it held for a hundred years. The beautiful drinking glasses of this period are collector items. English production was hindered only by a steady increase of taxation between 1745 and 1787 to pay for the war against France. The tax was levied on glass by weight, and as the tendency had been to add more lead oxide, the production was checked. As a result, many glassmakers moved to Ireland where glass was free from duty and glassworks were set up in Dublin and Waterford.

During the eighteenth and nineteenth centuries the British government regarded the glass industry as an inexhaustible fund to draw on in times of war and shortage. A glass duty was first imposed by statute in 1695 and made perpetual the following year, but it was so high as to discourage manufacture and was soon reduced by half. The duties were repealed in 1698 because of the reduction in the consumption of coal and the rise in unemployment. In 1746 duties were again levied, but they were also imposed on imported glassware. The Act of 1746 required a record to be kept of all furnaces, pots, pot chambers, and warehouses, and due notice to be given when pots were to be changed. In the same year the regulations were applied for the first time to Ireland, as a result of which many of the flourishing glassworks established there to avoid the excise duties began to decline. The duties seriously delayed technological innovation and in 1845 they were repealed. The industry immediately entered a new period of growth.

The Industrial Revolution started in England during the latter part of the eighteenth century, but this did not radically affect the glass industry in its early stages because mechanical power was not required in the glassworks. The impact of mechanization is shown best by its development in the American glass industry. American workers were scarce and wages were much higher than in Europe and so means were sought to increase productivity. One of the important developments at this time was a process for making pitchers by first pressing and then free-hand blowing, patented by Gillinder in 1865. This patent led to a period in which American container production changed from a craft industry to a mechanized manufacturing industry.

To the early glassmakers the nature of the structure of glass was a mystery. But they did know that the addition of certain components could modify properties. The most successful model used to describe the structure of oxide glasses is the random-network model devised by W.H. Zachariasen (1932). This model will be described in some detail in Chapter 21. Although the random-network model is over 60 years old it is still extensively used to explain the behavior and properties of oxide glasses and is widely used in industry in developing and modifying glass formulations.

2.9 BRIEF HISTORY OF REFRACTORIES

The development of refractories was important for many industries, most notably for iron and steel making and glass production. The iron and steel industry accounts for almost two-thirds of all refractories used. The discovery by Sidney Gilchrist Thomas and his cousin Percy Gilchrist in 1878 that phosphorus could be removed from steel melted in a dolomite-lined Bessemer converter (and subsequently on a dolomite hearth) was an important development. They solved a problem that had defeated the leading metallurgists of the day. And what is even more remarkable is that Thomas, who had originally wanted to be a doctor, was a magistrate's clerk at Thames police court in London. Out of interest he attended evening classes in chemistry, and later metallurgy, at Birkbeck Mechanics Institute (now Birkbeck College, University of London), where he became aware of the phosphorus problem. It took three attempts (over a 1-year period) by Thomas and Gilchrist to report the successful outcome of their work to the Iron and Steel Institute. A lesson in perseverance! When their paper was finally presented (Thomas and Gilchrist, 1879) the success of their process had become widely known and they attracted an international audience.

Dolomite refractories are made from a calcined natural mineral of the composition $CaCO_3 \cdot MgCO_3$. The production of magnesite, a more slag-resistant refractory than dolomite, began in 1880. Magnesite refractories consist mainly of the mineral periclase (MgO); a typical composition will be in the range MgO 83–93% and Fe_2O_3 2–7%. Historically, natural magnesite ($MgCO_3$) that was calcined provided the raw material for this refractory. With increased demands for higher temperatures and fewer process impurities, higher purity magnesia from seawater and brine has been used. This extraction process is described in Chapter 19.

In 1931 it was discovered that the tensile strength of mixtures of magnesite and chrome ore was higher than that of either material alone, which led to the first chrome–magnesite bricks. Chrome refractories are made from naturally occurring chrome ore, which has a typical composition in the range Cr_2O_3 30–45% Al_2O_3 15–33%, SiO_2 11–17%, and FeO 3–6%. Chrome–magnesite refractories have a ratio of 70 : 30, chrome : magnesia. Such bricks have a higher resistance to thermal shock and are less liable to change size at high temperatures than magnesite, which they replaced in open-hearth furnaces. The new refractories also replaced silica in the furnace roof, which allowed higher operating temperatures with the benefits that these furnaces were faster and more economical than furnaces with silica roofs.

Finally, not the least important development in refractories was the introduction of carbon blocks to replace fireclay (compositions similar to kaolinite) refractories in the hearths of blast furnaces making pig iron. Early experience was so successful that the "all carbon blast furnace" seemed a possibility. These hopes were not realized because later experience showed that there was sufficient oxygen in the upper regions of the furnace to oxidize the carbon and hence preclude its use there.

As in the history of other ceramics, the great progress in refractories was partly due to developments in scientific understanding and the use of new characterization methods. Development of phase equilibrium diagrams and the use of X-ray diffraction and light microscopy increased the understanding of the action of slags and fluxes on refractories, and also of the effect of composition on the properties of the refractories.

2.10 MAJOR LANDMARKS OF THE TWENTIETH CENTURY

Uranium dioxide nuclear fuel. In 1954 and 1955 it was decided to abandon metallic fuels and to concentrate upon UO_2 (sometimes referred to as urania) as the fuel for power-producing nuclear reactors. The water-cooled, water-moderated nuclear reactor would not have been possible without urania. The important properties are

1. Resistance to corrosion by hot water
2. Reasonable thermal conductivity, about 0.2–0.1 times that of metals
3. Fluorite crystal structure, which allows accommodation of fission products (see Section 6.5).

Reactor pellets are often cylinders, about 1 cm high and 1 cm in diameter, with a theoretical density of about 95%. Many pellets are loaded into a closely fitting zirconium alloy tube that is hermetically sealed before insertion into the reactor.

Following World War II (and the first use of nuclear weapons) there was a lot of research in the field of nuclear energy. Many of the people doing this research started with the wartime Manhattan project. Almost all worked in a few government-supported laboratories, such as those at Oak Ridge (in Tennessee) or Argonne (in Illinois) or at commercially operated laboratories that were fully government supported. In other countries most of the work was also carried out in government laboratories, for example, Chalk River in Canada and Harwell in England. The excitement in nuclear energy continued into the 1970s until the Three Mile Island incident. In the United States much of the interest and research in nuclear energy and nuclear materials have passed. Work continues in several countries including Japan, France, and Canada and will resume elsewhere as energy demands grow.

The float-glass process. Flat, distortion-free glass has long been valued for windows and mirrors. For centuries, the production of plate glass was a labor-intensive process involving casting, rolling, grinding, and polishing. The process required much handling of the glass and had high waste glass losses. As a result, plate glass was expensive and a premium product. Drawing processes were used extensively for window glass, but were not suitable for producing distortion-free sheets for the more demanding applications. In 1959 Alastair Pilkington introduced the float-glass process to make large unblemished glass sheets at a reasonable cost. It took 7 years and more than $11 M (over $150 M in 2006) to develop the process. We describe the technical details of the float-glass process in Chapter 21. Float-glass furnaces are among the largest glass-melting tank furnaces in use today and can produce 800–1000 tons of finished glass per day. A float-glass production line can be 700 feet long, with the tin path over 150 feet in length, and can produce a sheet with a width of 12 feet. The float-glass process dramatically decreased the cost of glass and led to a tremendous increase in the use of glass is modern architecture. Each year the float-glass process produces billions of dollars worth of glass.

Pore-free ceramics. During and following World War II new ceramics became important because of their special properties. They were fabricated from single-phase powders by sintering. This process differed from the classical silicate ceramic processing in that no liquid phase was formed. In the early stages of their development all such ceramics were porous after firing and hence opaque. Robert Coble found that the addition of a small amount of MgO would inhibit discontinuous grain growth in Al_2O_3 and permit it to be sintered to a theoretical density to yield a translucent product. The first commercial product using this new property was called Lucalox (for transLUCent ALuminum OXide). It is used primarily to contain the Na vapor in high-pressure Na-vapor lamps, which give nighttime streets their golden hue. Operating at high temperature, Na-vapor lamps have a luminous efficiency $>100\,\mathrm{lm\,W^{-1}}$, the highest of any light source (a 100-W tungsten-filament lamp has an efficiency of $\sim 18\,\mathrm{lm\,W^{-1}}$). They have displaced almost all other light sources for outdoor lighting. Na-vapor lamps are produced at an estimated rate of 16 million per year. A new product, the ceramic-metal halide lamp, utilizes the same ceramic envelope. It has an intense white light and is just now being introduced. Lumex Ceramic utilizes much of the same understanding in its preparation. It is based on doped yttrium oxide and is used as a scintillation counter in the GE computed tomography X-ray scanner.

Nitrogen ceramics. Silicon nitride was first produced in 1857 (Deville and Wöhler, 1857), but remained merely a chemical curiosity. It wasn't until much later that it was considered for engineering applications. During the period 1948–1952 the Carborundum Company in Niagara Falls, New York, applied for several patents on the manufacture and application of silicon nitride. By 1958 Haynes (Union Carbide) silicon nitride was in commercial production for thermocouple tubes, rocket nozzles, and boats and crucibles for handling molten metal. British work in silicon nitride, which began in 1953, was directed toward the ceramic gas turbine. It was supposed that sea and land transport would require turbines with materials capabilities beyond those of the existing nickel-based superalloys. This work led to the development of reaction-bonded silicon nitride (RBSN) and hot-pressed silicon nitride (HPSN). In 1971 the Advanced Research Projects Agency (ARPA) of the U.S. Department of Defense placed a $17 million contract with Ford and Westinghouse to produce two ceramic gas turbines, one a small truck engine and the other producing 30 MW of electrical power. The goal was to have ceramic engines in mass production by 1984. Despite considerable investment there is still no commercial ceramic gas turbine. The feasibility of designing complex engineering components using ceramics has been demonstrated and there has been increasing use of ceramics in engineering applications. Unfortunately there is no viable commercial process for manufacturing complex silicon nitride shapes with the combination of strength, oxidation resistance, and creep resistance required for the gas turbine, together with the necessary reliability, life prediction, and reproducibility.

Magnetic ferrites. The development of ceramic magnetic materials for commercial applications really started in the early 1930s. In 1932 two Japanese researchers Kato and Takei filed a patent describing commercial applications of copper and cobalt ferrites. J.L. Snoeck of N.V. Philips Gloeilampenfabrieken in Holland performed a systematic and detailed study of ferrites in 1948. This work launched the modern age of ceramic magnets. In the following year, Louis Néel, a French scientist, published his theory of ferrimagnetism. This was an important step in the history of magnetic ceramics because most of the ceramics that have useful magnetic properties are ferrimagnetic. About 1 million tons of ceramic magnets are produced each year.

Ferroelectric titanates. These materials are used as capacitors, transducers, and thermistors, accounting for about 50% of the sales of electroceramics. The historical roots leading to the discovery of ferroelectricity can be traced to the nineteenth century and the work of famous crystal physicists Weiss, Pasteur, Pockels, Hooke, Groth, Voigt, and the brothers Curie. Beginning with the work on Rochelle salt (1920–1930) and potassium dihydrogen phosphate (1930–1940), the study of ferroelectrics accelerated rapidly during World War II with the discovery of ferroelectricity in barium titanate. There then followed a period of rapid proliferation of ferroelectric materials including lead zirconate titanate (PZT), the most widely used piezoelectric transducer. Together with the discovery of new materials there was also an increase in the understanding of their structure and behavior, which led to new applications for ferroelectric ceramics, including microelectromechanical systems(MEMS).

Optical fibers. In 1964 Charles K. Kao and George A. Hockman, at the now defunct Standard Telecommunications Laboratory (STL) in the UK, suggested sending telecommunications signals along glass fibers. These early fibers had very high losses—the difference in the amount of light that went in versus the light that came out—compared to the fibers produced today. Robert Maurer, Donald Keck, and Peter Schultz at the Corning Glass Works in New York produced the first low-loss fibers in 1970. They were made by a chemical vapor deposition (CVD) process known as modified CVD (MCVD) and had losses <20 dB/km. Today, losses typically are 0.2–2.0 dB/km. In 1988 the first transatlantic fiberoptic cable, TAT-8, began carrying telephone signals from America to Europe. The link is 6500 km long and can carry 40,000 conversations per fiber. Glass fibers are also critical in today's endoscopes.

Glass ceramics. S. Donald Stookey made the first true glass ceramic at Corning Glass Works in 1957. He accidentally overheated a piece of Fotoform glass—a photosensitive lithium silicate glass. The glass did not melt, instead it was converted to a white polycrystalline ceramic that had much higher strength than the original glass. The conversion from the glass to the crystalline ceramic was accomplished without distortion of the articles and with only minor changes in dimensions. Small silver crystals in the glass acted as nucleation sites for crystallization. The development of this new Pyroceram composition launched Corning into the consumer products market. In 1958, Corningware® was launched. Stookey went on to develop a number of glass ceramics including one that was used as a smooth-top cooking surface for stoves. The invention of glass ceramics is a good example of serendipity. But Stookey had to be aware of the significance of what he had made. There are many other examples of the role of luck in the invention and development of new materials—Teflon, safety glass, and stainless steel.

Tough ceramics. Ceramics are inherently brittle with low toughness. In 1975 Garvie, Hannink, and Pascoe published a seminal article entitled "Ceramic Steel." They were the first to realize the potential of zirconia (ZrO_2) for increasing the strength and toughness of ceramics by utilizing the tetragonal to monoclinic phase transformation induced by the presence of a stress field ahead of a crack.

A great deal of effort has been expended since to devise theories and develop mathematical frameworks to explain the phenomenon. It is generally recognized that apart from crack deflection, which can occur in two-phase ceramics, the t → m transformation can develop significantly improved properties via two different mechanisms: microcracking and stress-induced transformation toughening. We describe these mechanisms in Chapter 18. So far three classes of toughened ZrO_2-containing ceramics have been made:

- Partially stabilized zirconia (PSZ)
- Tetragonal zirconia polycrystals (TZPs)
- Zirconia-toughened ceramics (ZTCs)

Bioceramics. The first suggestion of the application of alumina (Al_2O_3) ceramics in medicine came in 1932. But the field of bioceramics really did not develop until the 1970s with the first hip implants using alumina balls and cups. Studies showed that a ceramic ball was more biocompatible than metals and provided a harder, smoother surface that decreased wear. The Food and Drug Administration (FDA) in the United States in 1982 approved these for use. Each year about 135,000 hips are replaced in the United States; more than a million hip prosthesis operations using alumina components have been performed to date. Alumina is an example of a nearly inert bioceramic. Bioactive ceramics and glasses, materials that form a bond across the implant-tissue interface, were an important development. The first and most studied bioactive glass is known as Bioglass 45S5 and was developed by Larry Hench and coworkers at the University of Florida. The first successful use of this material was as a replacement for the ossicles (small bones) in the middle ear. A range of bioactive glass ceramics has also been developed.

Fuel cells. The British scientist Sir William Robert Grove (1839) discovered the principle on which fuel cells are based. Grove observed that after switching off the current that he had used to electrolyze water, a current started to flow in the reverse direction. The current was produced by the reaction of the electrolysis products, hydrogen and oxygen, which had adsorbed onto the Pt electrodes. Grove's first fuel cell was composed of two Pt electrodes both half immersed in dilute H_2SO_4: one electrode was fed with O_2 and the other with H_2. Grove realized that this arrangement was not a practical method for energy production. The first practical fuel cell was developed in the 1950s at Cambridge University in England. The cell used Ni electrodes (which are much cheaper than Pt) and an alkaline electrolyte. Pratt and Whitney further modified the alkaline fuel cell in the 1960s for NASA's Apollo program. The cells were used to provide on-board electrical power and drinking water for the astronauts. The alkaline fuel cell was successful but too expensive for terrestrial applications and required pure hydrogen and oxygen. There are many different types of fuel cell, but the one most relevant to ceramics is the solid-oxide fuel cell (SOFC). The SOFC uses a solid zirconia electrolyte, which is an example of a fast-ion conductor. We will discuss later how fuel cells convert chemical energy into electrical energy.

High-temperature superconductivity. High-temperature superconductivity was discovered in 1986 by Bednorz and Müller at the IBM Research Laboratory in Zurich, Switzerland. Art Sleight had shown earlier that oxides could be superconductors, but the required temperature was still very low. The discovery that certain ceramics lose their resistance to the flow of electrical current at temperatures higher than metal alloys may be as important as the discovery of superconductivity itself. Because of the significance of their discovery Bednorz and Müller were awarded the Nobel Prize for Physics in 1987, only a year after their discovery! The impact of the discovery of high-temperature superconductivity launched an unprecedented research effort. The 2-year period after Bednorz and Müller's discovery was a frenzied time with a host of new formulations being published. Paul Chu and colleagues at the University of Houston, Texas discovered the most significant of these new ceramics, $YBa_2Cu_3O_7$, in 1987. The YBCO or 123 superconductor, as it is known, is superconducting when cooled by relatively inexpensive liquid nitrogen. This opened up enormous possibilities and led to expansive speculations on a future based on these materials. The original promises have not been fulfilled. However, new applications are being developed and the field is still quite young. The current market is less than 1% of the advanced ceramics market. Predictions indicate that over the next 5 years annual growth rates up to 20% might be achieved.

2.11 MUSEUMS

There are many museums around the world that house collections of ceramics. The list that we give here is not exclusive, but it does include some of the major collections as well as sites that have important historical significance.

- Ashmolean Museum, Oxford, UK. This is a museum of the University of Oxford. Founded in 1683, it is one of the oldest public museums in the world. Important collections include early Chinese ceramics and Japanese export porcelain. www.ashmol.ox.ac.uk.
- British Museum, London. This is one of the greatest museums in the world. It contains a large and outstanding collection of antiquities including numerous Stone Age artifacts. www.thebritishmuseum.ac.uk.
- Corning Museum of Glass in Corning, New York. This is one of the outstanding glass collections in the world. Containing more than 33,000 objects representing the entire history of glass and glassmaking. www.cmog.org.
- Metropolitan Museum of Art in New York City, New York. Ceramic collections include Medici porcelain and Böttger porcelain. The museum also has one of the finest glass collections in the world. www.metmuseum.org.
- Musée du Louvre, Paris. This is one of the greatest museums of the world. It contains extensive collections of antiquities, including many examples of ancient earthenware vessels, some dating from the Chalcolithic period. www.louvre.fr.
- Musée National de Céramique at Sèvres, France. The collection includes examples of early European porcelains including a Medici porcelain bottle made in 1581; the first success in European efforts to produce ware equivalent to Persian and Chinese porcelain. It also contains examples of French soft-paste porcelain as well as earlier ceramics. www.ceramique.com.
- Ross Coffin Purdy Museum of Ceramics at the American Ceramic Society headquarters in Westerville, Ohio. It houses a cross section of traditional and high-tech ceramics produced in the last 150 years. www.acers.org/acers/purdymuseum.
- Smithsonian Institution. The Freer Gallery of Art and the Arthur M. Sackler Gallery contain collections of ancient ceramics with important examples from China and the Near East. www.asia.si.edu
- Victoria and Albert Museum, London. This is the world's largest museum of the decorative arts. It contains the National Collections of glass and ceramics. The extensive ceramic collection includes Medici porcelain and early Chinese and Near East ceramics. www.vam.ac.uk.
- Wedgwood Museum and Visitors Center in Barlaston, Stoke-on-Trent, UK. It contains many rare and valuable exhibits tracing the history of the company. It is also possible to tour the Wedgwood factory. www.wedgwood.com.
- The World of Glass in St. Helens, UK. This is a new museum and visitor center in the hometown of Pilkington glass. Pilkington plc originated in 1826 as the St. Helens Crown Glass Company. It contains the Pilkington glass collection. www.worldofglass.com.

2.12 SOCIETIES

There are several professional ceramics societies in the world. In the United States, the American Ceramic Society (ACerS) founded in 1899 is the principal society for ceramists. The society, which is based in Westerville, Ohio, is divided into 10 divisions: Art, Basic Science, Cements, Electronics, Engineering Ceramics, Glass & Optical Materials, Nuclear & Environmental Technology, Refractory Ceramics, Structural Clay Products, and Whitewares and Materials. The society organizes an annual meeting and publishes the *Journal of the American Ceramic Society*. The journal was created in 1918 and is one of the most important peer-reviewed journals in the field: www.acers.org.

Many other countries have professional societies for those working in the field of ceramics.

- Institute of Materials, Minerals and Mining (IoM^3) www.iom3.org
- Deutsche Keramische Gesellschaft www.dkg.de.
- European Ceramic Society (ECerS) www.ecers.org
- Swedish Ceramic Society www.keram.se/sks
- Ceramic Society of Japan www.ceramic.or.jp
- Canadian Ceramics Society www.ceramics.ca
- Chinese Ceramic Society www.ceramsoc.com
- Society of Glass Technology www.sgt.org

2.13 CERAMIC EDUCATION

The first formal ceramics program (Clay-Working and Ceramics) in the United States was established in 1894 at the Ohio State University in Columbus, Ohio. This marked a change from on-the-job training that was prevalent in the traditional North American art potteries and family establishments of earlier years toward a formal university study. Ceramics was also taught at Alfred University in New York, and many other schools across the nation. One of the most remarkable ceramists of the time was Adelaide Robineau, who taught at Syracuse University in New York. Robineau was a studio ceramist who devised her own clay bodies, concocted her own glazes, threw the forms, and decorated, glazed, and then fired them herself. Few women at the time were involved in the technical aspects of ceramic production. It was considered proper for women to be decorators only, rather than be part of more technical pursuits, or to throw on the wheel, a physically demanding job regarded as better left to men.

From 1894 to 1930 a number of universities formed their own ceramic engineering programs:

- New York State School of Clay-Working and Ceramics at Alfred University: 1900
- Rutgers University: 1902
- University of Illinois: 1905
- Iowa State College: 1906
- University of Washington: 1919
- West Virginia University: 1921
- North Carolina State University: 1923
- Pennsylvania State College: 1923
- Georgia Institute of Technology: 1924
- Missouri School of Mines (now University of Missouri–Rolla): 1926
- University of Alabama: 1928
- Massachusetts Institute of Technology: 1930

In the 1960s the first Materials Science departments began to appear in universities. Many of these were based on existing Metallurgy departments. In some of the universities that had specific ceramics programs, these activities were also incorporated into the new materials departments. Now, ceramic science and engineering is mostly taught in Materials Science and Engineering (MS&E) programs in the United States.

CHAPTER SUMMARY

The history of ceramics is intertwined with human history. From the first use of flint and obsidian during the Stone Age, the formation of vessels from clay, the use of refractories in the iron and steel industry, to the fabrication of optical fibers for high-speed communication ceramics have impacted society and technology in many ways. We mentioned many of the more recent developments in the field of ceramics. The science behind these materials will be described in many of the later chapters.

PEOPLE IN HISTORY

Aspdin, Joseph was an English mason and invented Portland cement in 1824. It was so named because of its resemblance to white limestone from the island of Portland, England. The first Portland cement made in the United States was produced at Coploy, Pennsylvania in 1872.

Bednorz, Johannes Georg (born 1950) and Karl Alexander Müller (born 1927) were scientists at the IBM research laboratory in Zurich, Switzerland, where they discovered the phenomenon of high-temperature superconductivity. They were both awarded the Nobel Prize for Physics in 1987. They began working together in 1982.

Böttger, Johann Friedrich was born in 1682. The young Böttger was apprenticed as an apothecary in Berlin where he claimed to have transformed mercury into gold, a feat he apparently demonstrated very convincingly in 1701. When reports of this reached Frederick I, Böttger fled to Saxony, where, in addition to his metallurgical researches, he began his work in ceramics. He used von Tschirnhaus' mirrors and lenses to produce a dense red stoneware and a European equivalent to white Chinese porcelain. He died in 1719. An authoritative history of Böttger and Meissen has been written by Walcha (1981).

Kingery, W. David. Kingery played a key role in creating the field of ceramic science. He was the author of *Introduction to Ceramics*, first published in 1960, the "bible" for a generation of ceramists. He was well known for his work in the field of sintering. In his later years he worked extensively on the history of ceramics. He died in June 2000.

Orton, Edward, Jr. was born in 1863 in Chester, New York. He studied mining engineering at Ohio State University (OSU). He was the founder of the ceramic engineering program at OSU in 1894 and a founder of the American Ceramic Society. He died in 1932.

Pilkington, Sir Alastair was born in 1920. He served in the Second World War. In 1942 he was captured on the island of Crete and spent the rest of the war as a POW. After finishing his studies at Cambridge University he joined the Pilkington glass company in 1947. By 1959 the float glass process was a success and the production of flat glass was revolutionized. He died in 1995.

Ravenscroft, George developed lead crystal glass during the last quarter of the seventeenth century to rival the Venetian *cristallo* developed during the early sixteenth century. He was granted a patent in March 1674 for a "crystalline glass resembling rock-crystal."

Seger, Hermann A. was the world's pioneer scientific ceramist. The English translation of Seger's work, *The Collected Writings of Hermann Seger*, was published in 1913 by the American Ceramic Society.

Simpson, Edward, better known as "Flint Jack," was an Englishman and one of the earliest experimental stone toolmakers. Using nothing more than a steel hammer he created replicas of ancient stone tools, which he sold in the late nineteenth century to museums and a Victorian public that was very interested in prehistoric times. He was able to make the tools appear old and worn by using chemicals and a lapidary tumbler. In 1867 he was sent to prison for theft.

von Tschirnhaus, Count Ehrenfried Walther was born in 1651. He was a physicist famous for his experiments with high temperatures and mineral fusions achieved by focusing sunlight in a solar furnace. He was made a foreign member of the French Royal Academy in 1683. He died in 1708.

Wedgwood, Josiah was born in 1730, the last child in a family of 12. He went into business for himself in 1759 in Staffordshire. One of the most remarkable innovators of the eighteenth century he revolutionized the process of manufacturing. He was a member of the Royal Academy and a member of the Lunar Society of Birmingham, which included in its members many of the great innovators of that period such as James Watt, the inventor of the steam engine. Mankowitz (1980) gives a detailed account of the life of Wedgwood and his pottery.

Zachariasen, William Houlder was born in 1906. He was a Norwegian-American physicist who spent most of his career working in X-ray crystallography. His description of the glass structure in the early 1930s became a standard. He died in 1979.

GENERAL REFERENCES

The American Ceramic Society, 100 Years (1998) The American Ceramic Society, Westerville, OH. A wonderfully illustrated history of the ACerS published to celebrate the societies centennial 1898–1998.

For the student with an interest in ceramic history the book by Kingery and Vandiver (1986) and the *Ceramics and Civilization* series edited by W.D. Kingery (1985, 1986), The American Ceramic Society, Westerville, OH are good resources. Volume I: *Ancient Technology to Modern Science* (1985). Volume II: *Technology and Style* (1986). Volume III: *High-Technology Ceramics—Past, Present, and Future* (1986).

Ceramics of the World: From 4000 B.C. to the Present (1991), edited by L. Camusso and S. Burton, Harry N. Abrams, Inc., New York. A beautifully illustrated history of ceramics with lots of historical details.

Douglas, R.W. and Frank, S. (1972) *A History of Glassmaking*, Fouls, Henley-on-Thames, Oxfordshire. The history of glassmaking is described and illustrated extensively. An excellent reference source.

Jelínek, J. (1975) *The Pictorial Encyclopedia of the Evolution of Man,* Hamlyn Pub Grp, Feltham, UK. Beautifully illustrated.

Kingery, W.D. and Vandiver, P.B. (1986) *Ceramic Masterpieces*, The Free Press, New York.

Lechtman, H.N. and Hobbs, L.W. (1986) "Roman Concrete and the Roman Architectural Revolution," in *Ceramics and Civilization III: High-Technology Ceramics—Past, Present, and Future*, edited by W.D. Kingery, The American Ceramics Society, Westerville, OH, pp. 81–128. This article gives a detailed historical perspective on this topic.

Levin, E. (1988) *The History of American Ceramics: 1607 to the Present*, Harry N. Abrams, Inc., New York. An illustrated history.

Schick, K.D. and Toth, N. (1993) *Making Silent Stones Speak: Human Evolution and the Dawn of Technology*, Simon & Shuster, New York.

SPECIFIC REFERENCES

Bednorz, J.G. and Müller, K.A. (1986) "Possible high T_c superconductivity in the Ba-La-Cu-O system," *Z. Phys. B—Condensed Matter* **64**, 189. The seminal paper describing "possible" high-temperature superconductivity in an oxide ceramic.

Deville, H. Ste.-C and Wöhler, F. (1857) "Erstmalige Erwähnung von Si_3N_4," *Liebigs Ann. Chem.* **104**, 256. Report of the first production of silicon nitride. Of historical interest only.

Garvie, R.C., Hannink, R.H., and Pascoe, R.T. (1975) "Ceramic steel?" *Nature* **258**, 703. The first description of the use of the tetragonal to monoclinic phase transformation for toughening ceramics.

Guillard, H.F. (1971) *Early American Folk Pottery*, Chilton Book Co., New York.

Kao, K.C. and Hockham, G.A. (1966) "Dielectric-fiber surface waveguides for optical frequencies," *Proc. IEE* **113**, 1151.

Lindsay, J. (1968) *The Ancient World: Manners and Morals*, Putnam, New York.

Mankowitz, W. (1980) *Wedgwood*, 3rd edition, Barrie and Jenkins, London. A standard biography of Josiah Wedgwood.

Moseley, C.W.R.D. (translated by) (1983) *The Travels of Sir John Mandeville*, Penguin Books, London, p. 57. Describes the Fosse of Mynon in Acre, a Syrian seaport on the Mediterranean.

Thomas, S.G. and Gilchrist, P.G. (1879) "Elimination of phosphorus in the Bessemer converter," *J. Iron Steel Inst.* **20**. A landmark paper that led to important changes in the steel making industry and also to the development of new types of refractory.

Walcha, O. (1981) *Meissen Porcelain*, translated by H. Reibig, G.P. Putnam's Sons, New York. A history of Böttger and Meißen based in large part on archival studies at Meißen.

Wood, N. (1999) *Chinese Glazes*, A&C Black, London. A beautifully illustrated book showing the early Chinese genius for ceramics.

Wu, M.K., Ashburn, J.R., Torng, C.J., Hor, P.H., Meng, R.L., Gao, L., Huang, Z.J., Wang, Y.Q., and Chu, C.W. (1987) "Superconductivity at 93 K in a new mixed-phase Y-Ba-Cu-O compound system at ambient pressure," *Phys. Rev. Lett.* **58**, 908. The first description of superconductivity at liquid-nitrogen temperature.

Zachariasen, W.H. (1932) "The atomic arrangement in glass," *J. Am. Chem. Soc.* **54**, 3841. Describes a model for the structure of oxide glasses that has become a standard for these materials.

EXERCISES

2.1 Gypsum, the raw material for Plaster of Paris, occurs in several varieties. The Greeks used a form of gypsum as windows for their temples. What particular property would be important for this application? What form of gypsum would be most suitable?

2.2 What do you think might be the role of CuO in the Han lead glaze (Table 2.2)?

2.3 Why do you think it was so important for the early ceramic industries to locate near the source of raw materials? Does a similar situation occur today?

2.4 The largest concrete construction project in the world is the Three Gorges Dam in China. How much concrete is used in this project?

2.5 Which company is the largest producer of glass optical fibers?

2.6 Corningware® is a glass ceramic product that was once widely used for cookware, but is rarely used now. What were some of the problems with Corningware® and would these problems be inherent to all glass ceramics?

2.7 Solid oxide fuel cells (SOFC) are not being used in transportation applications (such as automobiles and buses). What fuel cells are being used for these applications and what are their advantages over the ceramic-based SOFCs?

2.8 The transition temperature (T_c) for the YBCO superconductor is 95 K. Higher T_cs are found with other ceramic high-temperature superconductors, but these materials are not being used commercially. What are some of the other materials and what are some of the factors that are limiting their use?

2.9 The Hall of Mirrors (La Galerie des Glaces) at the Palace of Versailles in France was begun in 1678, well before the development of the float glass process. What technology was available in the seventeenth century for producing flat plates of glass?

2.10 Concrete is a mixture of gravel (called aggregate) and cement. The spectacular 142-foot internal diameter dome of the Pantheon in Rome is made of concrete. What material did the Romans use for aggregate in the construction of the Pantheon? Could the material they used be classified as a ceramic?