9

Furnaces

CHAPTER PREVIEW

Furnaces are the essential equipment in any ceramics laboratory. They can range in size from small electrically heated box furnaces, often called muffle furnaces, which can fit on a bench to the enormous gas-fired furnaces used to melt glass. In between these extremes there are furnaces of many shapes and sizes, designed to run at a range of temperatures and in a range of atmospheres. In addition to obtaining a high temperature, it is necessary to have furnace components that can withstand these temperatures without degradation. These materials are known as refractories. Much of our knowledge of refractory ceramics has come from early developments in the iron and steel industries. Whenever temperatures are high, vapor pressures may also be high, so be aware that the furnace material may contaminate the material you are processing. We also describe methods for measuring high temperatures and some of the important safety considerations that you must know when using furnaces and working at high temperatures.

9.1 THE NEED FOR HIGH TEMPERATURES

There are many areas in ceramics where we need high temperatures.

- Sintering—Most bulk ceramic components are made by sintering a powder compact. We need to use high temperatures (>1,200°C) because of the low self-diffusion coefficients in the solid state. Even for liquid phase sintering, temperatures are still often >1,200°C.
- Reactions—Forming mixed metal oxides such as $BaTiO_3$ and $NiAl_2O_4$ by solid-state reaction of the component oxides requires the use of elevated temperatures.
- Phase Transformations—An important phase transformation is that involving crystallization of a glass to form a glass-ceramic. Although the temperatures involved are not as high as those needed for glass melting, the phase transformation is typically carried out at around 800°C. Control of temperature is often necessary to ensure that the desired crystalline phase is formed and in the optimum particle size.
- Glass Melting—Glass products form the largest single segment of the ceramics industry. Glass production frequently requires melting of a batch consisting of a mixture of powdered metal oxides and metal carbonates. The temperature necessary to form a homogeneous liquid melt varies with batch composition but is typically in the range 1,300–1,600°C. The melt is also very corrosive, which provides additional considerations in the choice of refractories.
- Crystal Growth—Most of the methods used to form single crystals, whether in the laboratory or in industry, require the use of high temperatures. Many single crystals are produced from the melt or by using suitable fluxes, and particular attention has to be paid to avoiding contamination of the melt and controlling the temperature during growth.

9.2 TYPES OF FURNACE

We can categorize the furnaces used to fire and sinter ceramic components in several ways. One way is based on the type of heat source used:

- Combustion
- Resistive
- Microwave, radiofrequency (RF), or infrared (IR)/visible light

Alternatively we could group them as:

- Periodic or batch furnaces
- Continuous furnaces

Electrical furnaces can produce direct (resistive) or indirect (induction or microwave) heating. We look at the

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characteristics of each group of furnaces, keeping in mind that there is overlap. For example, we can have continuous gas-fired furnaces or continuous electrically fired furnaces. Historically, continuous furnaces and gas-fired furnaces are usually found in industry. Batch and electrically fired furnaces are used widely in university laboratories and in many small to medium-sized industrial applications. The current trend toward more environmental controls and demand for higher quality continues to expand the applications for electrically powered furnaces. Electric furnaces account for about 60% of the total industrial heating equipment market (about $3 billion in total). There is still growth in the use of combustion furnaces, in particular for applications in the metal and cement industries.

This chapter is called furnaces, but it could have been called kilns or ovens as these terms are used to describe many of the same types of equipment. "Kiln" is widely used in the traditional ceramics industry and the pronunciation is sometimes "kil." In the Potteries in England, for example, you may encounter the alternative pronunciation. "Furnace" is used interchangeably with kiln. "Oven" is more often used for either equipment used for drying ceramics (typically using lower temperatures) or for small furnaces.

9.3 COMBUSTION FURNACES

The most common combustion furnaces used in ceramic processing are gas-fired and use gaseous hydrocarbons as fuel. The large amount of energy produced heats the furnace and the parts inside. Gas-fired furnaces are used mainly in large industrial applications such as glass melting, the production of ceramic colors, and firing of traditional ceramic articles (e.g., tiles and whiteware). Figure 9.1 shows an example of a commercial glass-melting furnace.

FIGURE 9.1. Gas-fired batch furnace used in a commercial glass-blowing operation.

Combustion is an oxidative process; for the case where methane is the fuel:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad (9.1)$$

The standard molar enthalpy, or heat, of combustion (ΔH_c^o) may be calculated using equation 9.2.

$$\Delta H_c^o = \sum \Delta H_f^o(\text{products}) - \sum \Delta H_f^o(\text{reactants}) \qquad (9.2)$$

For the reaction given in equation 9.1 we can write

$$\Delta H_c^o = \Delta H_f^o(CO_2) + \Delta H_f^o(2H_2O) - [\Delta H_f^o(CH_4) + \Delta H_f^o(2O_2)]$$

where ΔH_f^o refers to the enthalpy of formation. These values are tabulated for many substances. One source is the thermochemical tables (e.g., Barin 1997). Making the appropriate substitutions, we get

$$\Delta H_c^o = -393.51 + 2(-285.83) - (-74.81) = -890.36 \text{kJ/mol}$$

(Note that ΔH_f^o for a material in its standard state is zero).

The simple idea is that the amount of energy released during combustion depends on the strength of the bond in the gas. Fuels with many weak (less stable) bonds, such as C–C and C–H, yield more energy than fuels with fewer such bonds or fuels that contain large numbers of strong bonds (e.g., C–O and O–H). Table 9.1 lists the standard molar enthalpies of combustion for a range of hydrocarbons.

For many combustion reactions, the standard enthalpy changes are listed as a function of temperature. If this information is not available, then it is necessary to calculate the enthalpy change at the temperature of interest, $\Delta H_c^o(T)$, using equation 9.3.

$$\Delta H_c^o(T) = \Delta H_c^o(298) + \int_{298}^{T} \Delta c_p dT \qquad (9.3)$$

TABLE 9.1 Standard Molar Enthalpies of Combustion, ΔH_c^0 (kJ/mol)

CH_4 (g)	890
C_2H_2 (g)	1,300
C_2H_4 (g)	1,411
C_2H_6 (g)	1,560
C_4H_{10} (g)	2,877
C_6H_{12} (*l*)	3,920
C_6H_{14} (*l*)	4,163
C_6H_6 (*l*)	3,268
$C_{10}H_8$ (s)	5,157
CH_3OH (*l*)	726
CH_3CHO (g)	1,193
CH_3CH_2OH (*l*)	1,368
CH_3COOH (*l*)	874
$CH_3COOC_2H_5$ (*l*)	2,231
C_6H_5OH (s)	3,054

TABLE 9.2 Temperature Dependence of Heat Capacities, $C_{p,m}$

Gases (298–2,000 K)	*a* (JK^{-1} mol^{-1})	*b* (10^{-3} JK^{-2} mol^{-1})	*c* (10^{5} $JKmol^{-1}$)
H_2	27.28	3.26	0.50
O_2	29.96	4.18	−1.67
CO_2	44.23	8.79	−8.62
H_2O	30.54	10.29	0
CH_4	23.64	47.86	−1.92

TABLE 9.3 Adiabatic Flame Temperatures of Various Gas Mixtures

	Fuels with air		*Fuels with O_2*	
Gas	*K*	*°C*	*K*	*°C*
H_2	2,450	2,177	3,395	3,122
CH_4	2,276	2,003	3,849	3,576
C_2H_2	2,657	2,384	3,737	3,464

where c_p is the molar heat capacity at constant pressure, which can be expressed in the form

$$c_p(T) = a + bT + cT^{-2} \tag{9.4}$$

The temperature-independent coefficients a, b, and c are listed for several species in Table 9.2. It is important to remember that a, b, and c are only valid over certain temperature ranges.

Thermodynamics determines the maximum amount of energy that can be produced by a combustion reaction. This can be quantified by what is known as the adiabatic flame temperature, which is shown for several possible gas mixtures in Table 9.3. These values, and those for other gas mixtures, can be calculated by solving the enthalpy balance (Kirchhoff's law)

$$\Delta H_c^{o}(298\text{K}) + \int_{298\text{K}}^{T} \Sigma c_p dT = 0 \tag{9.5}$$

The maximum temperature that can be achieved in a gas-fired furnace is well below the adiabatic flame temperature because of heat loss caused by incomplete combustion and dissociation of the combustion gases (an endothermic process) at high temperature. Heat is also lost by conduction through the refractories and imperfect insulation.

9.4 ELECTRICALLY HEATED FURNACES

Most electrically heated furnaces use the principle of Joule, or resistance, heating where current flowing through a resistor produces heat. The starting point is Ohm's law:

$$V = IR \tag{9.6}$$

relating the current, I, through a resistance, R, to the applied potential, V. As current flows, power (P) is dissipated.

$$P = VI = I^2R \tag{9.7}$$

What we are often most interested in is the amount of energy converted into heat, Q, which is obtained simply by multiplying P by time, t.

$$Q = RI^2t = \rho\frac{l}{A}I^2t \tag{9.8}$$

The units of Q are joules but are often given as kWh (kilowatt hour), the familiar unit used by power utility companies to determine electricity usage.

The heat source in the earliest electric furnaces was direct current (dc) arcs formed between carbon electrodes, so the heating element really was an element. Carbon (in the form of graphite) is still used as a heating element, but most heating elements are now made from compounds. There are several types of heating element. We describe some of the important ones in Section 9.7. The choice of heating element depends on the maximum temperature that is required and the environment that the element will be exposed to.

There are several advantages to electric heating:

- It's easy to measure power input
- It's easy to control heating rates and temperature
- The furnace can operate in an atmosphere independent of the heating source

The main disadvantage of electric heating is that it usually costs more per energy unit than gas heating. However, the total energy usage for electric furnaces may often be lower than for gas-fired furnaces. The cost issue is not normally a problem in a university laboratory, but it can be a major concern for industrial applications. Two other types of furnace that use electricity are induction furnaces and microwave furnaces.

9.5 BATCH OR CONTINUOUS OPERATION

Batch operation. Figure 9.2 shows an example of a small electrically heated batch furnace. These types of furnace are used for temperatures up to 1,800°C and are designed

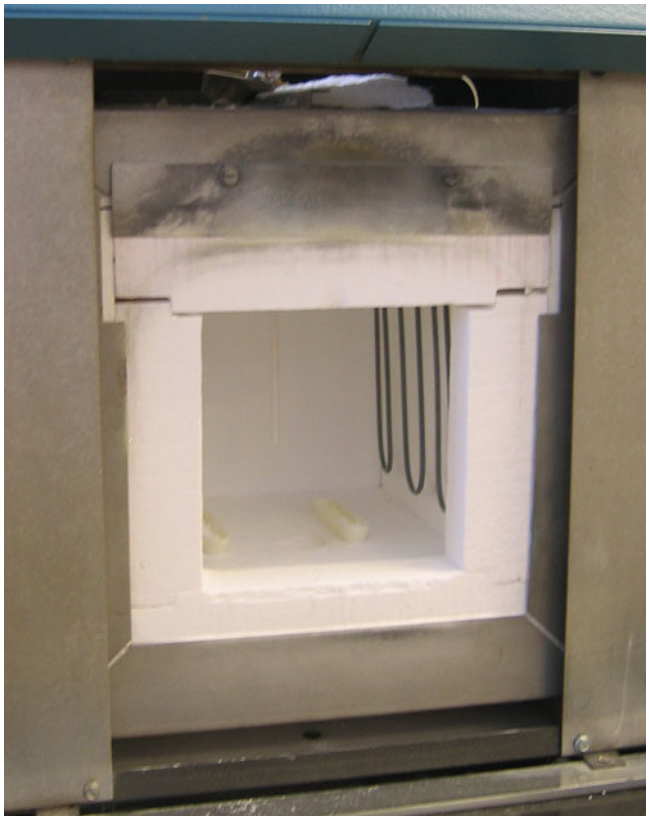

FIGURE 9.2. Small electrically heated box furnace.

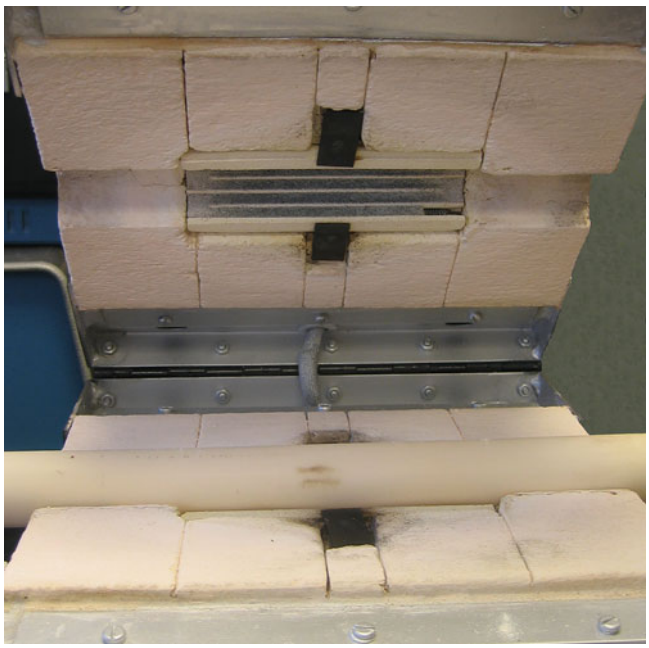

FIGURE 9.3. Electrically heated tube furnace.

to be used in air. Figure 9.3 shows another example of a batch furnace. This particular furnace is known as a tube furnace. By flowing gases along a tube placed inside the furnace, the heating environment can be controlled. The usual operation of a batch furnace involves inserting the ceramic parts into the furnace at room temperature, heating to the desired temperature, then cooling back to room temperature. In some cases,

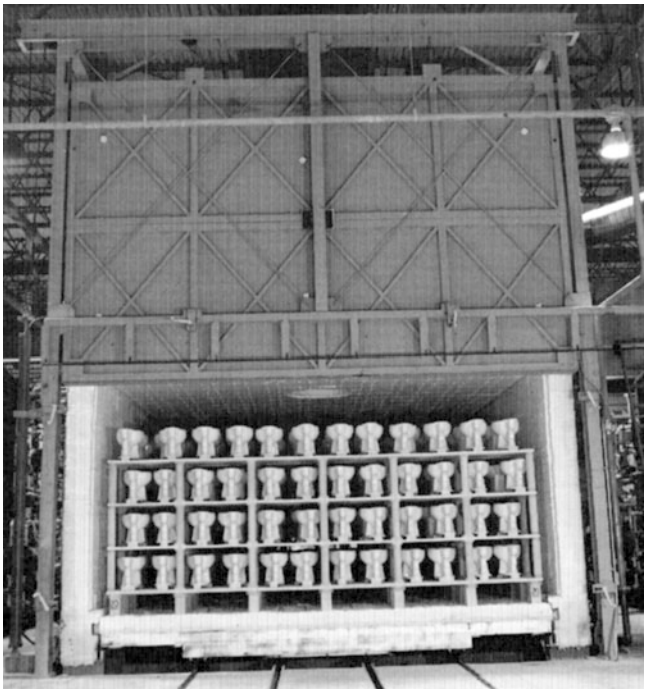

FIGURE 9.4. Large batch furnace used in the production of traditional ceramic products.

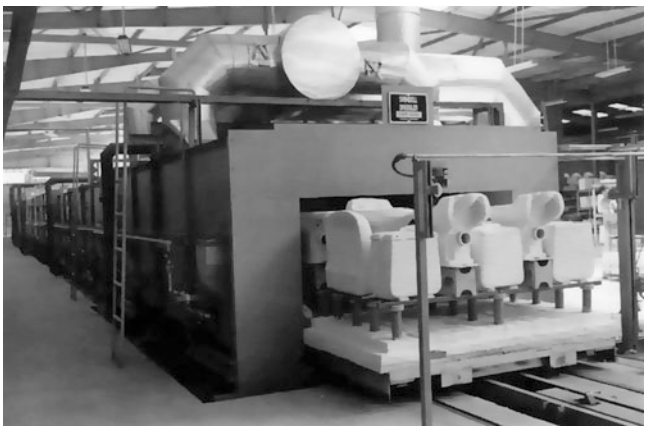

FIGURE 9.5. Large continuous furnace used in industry to produce traditional ceramic products and advanced ceramics, such as multilayer chip capacitors.

the parts may be inserted and removed while the furnace is at high temperature. For powders, this approach does not usually produce any problems, but for large consolidated parts the problem of cracking due to thermal shock is an important consideration. Batch furnaces are mainly used for small-scale heating experiments and for process development and evaluation; but they can also be found in large industrial applications, as shown in Figure 9.4. The advantages of batch furnaces are that they are simple to operate and flexible.

Continuous operation. Figure 9.5 shows an example of a large industrial continuous furnace. The classic use is for firing bricks, pottery, tiles, and whitewares. Similar furnaces are used in the production of advanced ceramics such as multilayer ceramic chip capacitors.

In a continuous furnace, the temperature at each location in the furnace is constant with time. The parts are moved through the furnace at a velocity giving the desired time–temperature profile. Continuous furnaces are best for mass production, where large quantities of material are subjected to the same conditions. The disadvantages of continuous furnaces are that the furnace temperature must be maintained throughout the process and there is a lack of flexibility.

9.6 INDIRECT HEATING

Induction furnaces. Induction heating provides a means for precise heating of electrically conducting objects. The object is immersed in an alternating magnetic field, which is usually produced by an external coil energized by an alternating current (ac) source. The magnetic field induces voltages in the conductive material, and these voltages produce circulating currents (called eddy currents). The magnitude of the induced voltage and the impedance of the material determine the size of the induced currents. It is the flow of induced currents that produces Joule heating of the material. A piece of metal may be introduced to begin the heating process—we must be able to couple the applied field to the ceramic. If the material we want to heat is an insulator, we can place it inside a conductive crucible, such as graphite. A typical induction furnace is shown in Figure 9.6.

FIGURE 9.6. Induction furnace. The sample is mounted within the coils, which are usually water-cooled copper.

Induction heating gives many advantages:

- It is clean and fast.
- The process is easily reproducible.
- It can be automated.
- Localized heating is possible (actually, it's essential).

Induction furnaces operate at frequencies of 60–1,000 Hz and are thus often referred to as radio-frequency (RF) furnaces. They can be used for obtaining temperatures up to 3,000°C. Because the coil currents may be as high as 15 kA, the Cu coil conductors are usually hollow to permit water circulation for cooling.

Induction furnaces are generally used for melting and surface hardening. They are sometimes used for sintering in conjunction with hot pressing. These are the furnaces used in the skull-melting process, which is used to produce cubic zirconia.

Microwave furnaces. Microwave heating is an application of induction heating using higher frequencies. In many ways microwave furnaces are just expensive microwave ovens.

Heat is generated in nonconducting materials when microwave radiation excites the molecules in the material. The high-frequency radiation causes molecular polarization, and the ability of the molecules to follow the rapid reversal of the electric field results in the conversion of electromagnetic energy into heat within the irradiated material. The two predominant frequencies are 915 and 2,450 MHz (the microwave region extends from about 1 GHz up to about 300 GHz). Household microwave ovens operate typically at 2,450 MHz. The main difference between the microwave oven you use at home and those used in industrial applications is the power. The maximum power of a domestic appliance is about 700 W; industrial versions have powers up to 5 kW.

Microwave furnaces currently are used for research and small-scale production because the available power sources are limited in size. Microwave processing is an area where considerable research is being performed. The main direction for this research, and the possibility for future commercial applications, is reduction of production times and lowering the amount of energy consumption required for part processing.

The term "microwave safe" is used for various ceramic, glass, and plastic food and beverage containers. All glass and glass-ceramic cookware is microwave safe because it can withstand the high temperatures that can occur when cooking foods that are high in fat or sugar. Many plastics don't satisfy this requirement.

Arc-image furnaces. This usage is comparable to heating with electric-light bulbs. The light is focused on the sample using ellipsoidal mirrors. The heat is clean, and the sample can be held in an inert or oxidizing atmosphere. An important application of arc-image furnaces is in the growth of single crystals of ceramics with high melting temperatures (Chapter 29).

Lasers and electron beams. These can be used to provide local heating or for heating small quantities. The temperature control is not great, but these techniques are very versatile. Electron beams are used to vaporize silicon for thin-film deposition using molecular-beam epitaxy. A focused laser beam is the basis of the pulsed-laser deposition (PLD) thin-film growth technique (Chapter 28).

9.7 HEATING ELEMENTS

Never use a furnace like a black box. The heating elements will go to certain temperatures, but even then you may not want that type of material close to your sample to minimize contamination. Table 9.4 lists the materials used for electrical resistance heating.

- Furnaces operating in air at temperatures up to 1,300°C usually use wire-wound Cr alloys.
- For higher temperatures in air, either precious metals or SiC rods are used.
- For very high temperatures requiring an oxidizing environment, ceramic elements, most commonly ZrO_2, are used.
- In cases where reducing atmospheres can be tolerated, graphite or refractory metals such as Mo and W can be used.

We now look, in a little more detail, at some of the ceramic materials that are used as heating elements in furnaces. We also mention one other type of resistance element, SnO_2, which is used in electrically heated glass-melting furnaces.

TABLE 9.4 Electrical Resistance Heating Element Materials

Material	*Maximum useful temperature (°C)*	*Usable atmosphere*
Chromium alloys		
Chromel C, Nichrome, Kanthal DT	1,100	ONR
Kanthal A, Chromel A	1,300	ONR
Metals		
Pt	1,400	ONR
Pt-Rh alloys	1,500–1,700	ONR
Mo	1,800	NR
W	2,800	NR
Ceramics		
SiC	1,500	ON
$MoSi_2$	1,700	ON
Lanthanum chromite	1,800	O
Thoria, stabilized	2,000	ONR, shock
Zirconia, stabilized	2,800	ONR, shock
Graphite	3,000	NR

O oxidizing, *N* neutral, *R* reducing, *Shock* particularly poor resistance to thermal shock

9.7.1 Silicon Carbide

Silicon carbide is the most widely used nonoxide ceramic for heating elements in high-temperature furnaces. SiC heating elements can be used up to 1,500°C in air because of the formation of a protective oxide layer. At temperatures in the range 1,500–1,600°C, SiC decomposes.

$$SiC\ (s) + O_2(g) \rightarrow SiO\ (g) + CO\ (g) \qquad (9.9)$$

There are three main methods used to produce SiC heating elements:

- In situ reaction
- Reaction bonding
- Sintering

In the first method, a carbon tube is heated to about 1,900°C in a bed of sand (SiO_2) and coke (C). The tube may be directly resistance heated or heated indirectly by a sacrificial tube of smaller diameter. Silicon monoxide is generated from reaction 9.9 and infiltrates the carbon tube transforming it to SiC. The SiC tube is then removed and the residual carbon burned out. The tube has a porosity of about 30% and a large internal surface area. To prevent internal oxidation during use, the outer surfaces of the tube are coated with a thin layer of a calcium aluminosilicate glass and then fired at about 1,450°C. In this form, the tubes have uniform resistance along their length. A higher-resistance heating section is made by diamond sawing a spiral through the tube wall, as shown in Figure 9.7. Adjusting the pitch of the cut varies the resistance.

In the second method, a mix of SiC and carbon powders and a polymer binder is extruded to a rod. The "green" form is then brought in contact with molten silicon. The liquid penetrates the pores, reacting with the carbon to form silicon carbide and bonding the grains together. The resulting ceramic has low porosity and consequently a long service life. The resistance of the hot section of the rod is adjusted to the required value by spiraling, which is easier to do when the ceramic is in the "green" state.

In the third method, SiC powder is mixed with a polymer binder and extruded. The rod is then sintered in a carbon furnace at approximately 2,300°C. To give the rod low-resistance terminations, the ends are dipped into molten silicon, which is allowed to infiltrate along a predetermined length. In all cases, the ends of the elements are coated with aluminum to make electrical contacts.

The main disadvantage of silicon carbide heating elements is that they are extremely brittle and must be handled carefully, especially when being installed and wired.

9.7.2 Molybdenum Disilicide

Many metals form conductive silicides that, like SiC, are resistant to oxidation through the formation of stable layers

FIGURE 9.7. Examples of SiC furnace elements.

of silicates or silica on their surfaces at high temperatures. Molybdenum disilicide ($MoSi_2$) has been developed as a heating element for use in air at temperatures >1,500°C. The resistivity of $MoSi_2$ behaves in the same way as for a metal—it increases with increasing temperature. The room-temperature resistivity of $MoSi_2$ is 2.5×10^{-7} Ω-m; it increases to about 4×10^{-6} Ω-m at 1,800°C.

A commercial $MoSi_2$ heating element, known as Kanthal Super, comprises a mixture of $MoSi_2$ particles bonded together with an aluminosilicate glass phase, which forms 20% of the total volume. The elements are fabricated by extruding a mixture of fine $MoSi_2$ powder with clay. The rods are dried, sintered, and cut to various lengths. The heating zones are bent to the required shape at high temperature and are then welded to the larger-diameter terminal sections. The best-grade $MoSi_2$ element is capable of operating up to 1,800°C.

9.7.3 Zirconia

Cubic stabilized zirconia (ZrO_2) is used as a furnace element, allowing temperatures >2,000°C to be achieved. Because of the low conductivity of ZrO_2 at room temperature, they require preheating by gas or conventional resistance elements to reduce the resistance to a level at which Joule heating is effective. At temperatures >1,000°C, the ceramic becomes sufficiently conductive to be self-heating. Zirconia can also be used as a susceptor for induction heating.

9.7.4 Tin Oxide

SnO_2 is frequently used as electrodes in glass melting furnaces, particularly those used for making glasses for optical components and lead "crystal" tableware. The requirements for the electrode material are very specific:

- Electrical conductivity must be high at glass-melting temperatures.
- Resistance to corrosion by the molten glass must be high.
- It should not discolor the glass.

The electrodes are formed by mixing SnO_2 powder with small amounts of sintering aids such as ZnO and CuO and additives such as Sb and As, which make the material semiconducting. Typical electrode compositions contain more than 98 wt% SnO_2. The oxide powders, together with binders, are pressed or slip cast into cylinders and fired in oxidizing conditions at temperatures of approximately 1,400°C. The largest electrodes made in this way are in the form of cylinders 600 mm long and 150 mm in diameter weighing about 60 kg. Cooling from the sintering temperature is carried out, in part, in a nitrogen atmosphere with the object of creating oxygen vacancies and so increasing room-temperature conductivity, which is typically about 0.1 S/m. High conductivity minimizes Joule heating in the electrode region outside the molten glass.

In electrically heated glass-melting furnaces, the batch is preheated, using oil or gas, to about 1,000°C, when it has sufficient conductivity to be directly heated to the "glass-fining" temperature (1,300–1,600°C) by power dissipated internally. By supplying the heat from within the body of the glass melt rather than from the outside, the free surface temperature is kept relatively low, and loss of volatile elements, particularly lead, is avoided. The process is economic because the heat is generated where it is required (i.e., in the glass). The elements are resistant to attack by glass and last about 2 years before being replaced.

9.7.5 Graphite

Graphite is a good choice as a heating element for resistive heating because it has a high melting temperature and a very low vapor pressure, even at temperatures above 3,000°C. These characteristics led to the use of graphite filaments in early incandescent lamps (They were eventually replaced by tungsten, which came into general use as a filament for incandescent lamps in 1911). The major disadvantages of using graphite furnace elements are:

- Reactivity with oxide ceramics
- Susceptibility to oxidation

All metal oxides are reduced when in direct contact with graphite at high temperatures. Even the most refractory oxides are reduced if the temperature is high enough.

9.7.6 Molybdenum and Tungsten

Both molybdenum and tungsten are refractory metals and are used as heating elements. Molybdenum reacts with oxygen at >700°C to form molybdenum trioxide (MoO_3). For applications above this temperature, it is necessary to have a reducing environment or vacuum. The maximum usable temperature for molybdenum heating elements is about 1,500°C. Above this temperature, creep is a problem. Tungsten can be used for temperature up to 3,000°C in inert atmospheres.

Figure 9.8 illustrates a problem that can occur with any furnace element—sample contamination. The sample is α-SiC that was heated in a tungsten furnace for 12 h at 1,300°C. The dark features are tungsten particles evaporated onto the surface during heat treatment.

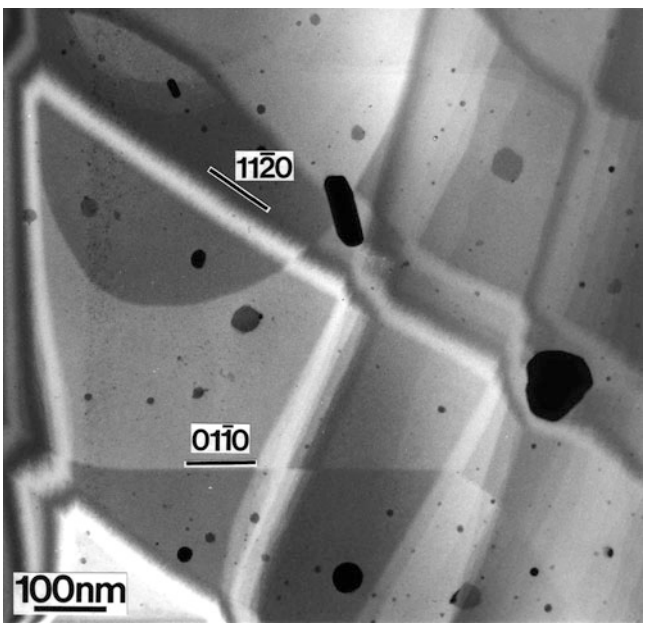

FIGURE 9.8. A TEM image showing small particles of tungsten contamination formed on SiC.

9.8 REFRACTORIES

Refractories are materials capable of withstanding high temperatures and not degrading in a furnace environment when in contact with corrosive liquids and gases. Refractory insulators are used in high-temperature applications to reduce heat losses and to save fuel. Table 9.5 lists some of the important furnace insulation materials together with their maximum usable temperature and thermal conductivity, k. The lower the value of k, the better is the thermal insulating effect for equal thickness.

Figure 9.9 shows the arrangement of refractory bricks in a typical glass-melting furnace. Approximately 70% of all refractories used by industry are in the form of preformed bricks that come in a variety of shapes. There are several different types of refractory brick, and the choice depends mainly on the maximum operating temperature of the furnace and on the size of the furnace.

- Silica brick. Made from naturally occurring sources of silica and bonded by adding 3.0–3.5% CaO to promote liquid phase sintering.
- Semisilica brick. A silica brick containing 18–25% Al_2O_3.
- Fireclay brick. Made from kaolinite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$) with 25–45% Al_2O_3.

TABLE 9.5 Refractories for Thermal Insulators

Material	T_{max} (°C)	k ($Wm^{-1}\,K^{-1}$)
Glass, fiber	600	0.05
SiO_2, fiber	1,000	0.17
Firebrick, insulating	1,200–1,500	0.52
Fiberfrax	1,650	0.12
Al_2O_3, bubble	1,800	1.04
MgO, powder	2,200	0.52
MgO, solid	2,300	2.94
Carbon or graphite, powder	3,000	0.09
Radiation shields, Mo	2,100	0.69

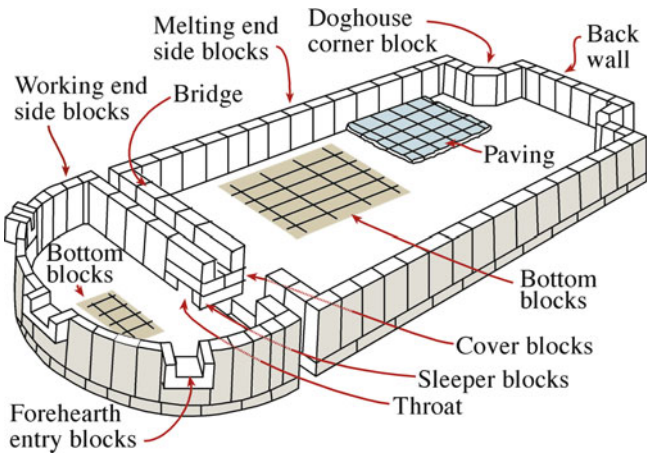

FIGURE 9.9. Layout of refractories in an industrial glass melting furnace.

- High-alumina brick. Alumina content in the range 45–100 wt.%.
- Dolomite brick. Made from dolomite ($CaCO_3 \cdot MgCO_3$).
- Magnesia brick. Contains mainly MgO (typically >90% MgO).
- Chrome brick. Made from naturally occurring chrome ore. Contains 34% Al_2O_3 and 30% Cr_2O_3. Often MgO is added to produce chrome-magnesia brick.
- Zircon refractory brick. Zircon is $ZrO_2 \cdot SiO_2$. Bricks may contain 4% CaO.

The schematic diagram of a blast furnace in Figure 9.10 shows how different types of refractories are used within the furnace. The maximum temperature (>1,700°C) is reached toward the base of the furnace, where the air "blast" comes in and where the slag is formed. Slag is a glassy waste product made up of limestone and silica (impurities in the iron ore), ash, and oxides. It is lighter than the molten iron and so forms a layer above it.

Refractories are one example of where a high-density ceramic product is not desirable—the space-shuttle tiles being the extreme example. The thermal conductivity, k_p, of air is only 0.026 $Wm^{-1}K^{-1}$, significantly less than that of most crystalline ceramics. The thermal conductivity of a porous ceramic can be calculated using equation 9.10.

$$k_m = k_c\left(\frac{1+\{2V_p[1-(k_c/k_p)]/[(2k_c/k_p)+1]\}}{1-\{V_p[1-(k_c/k_p)]/[(k_c/k_p)+1]\}}\right) \quad (9.10)$$

where k_c is the thermal conductivity of the ceramic; k_p is the thermal conductivity of air; and V_p is the volume fraction of porosity.

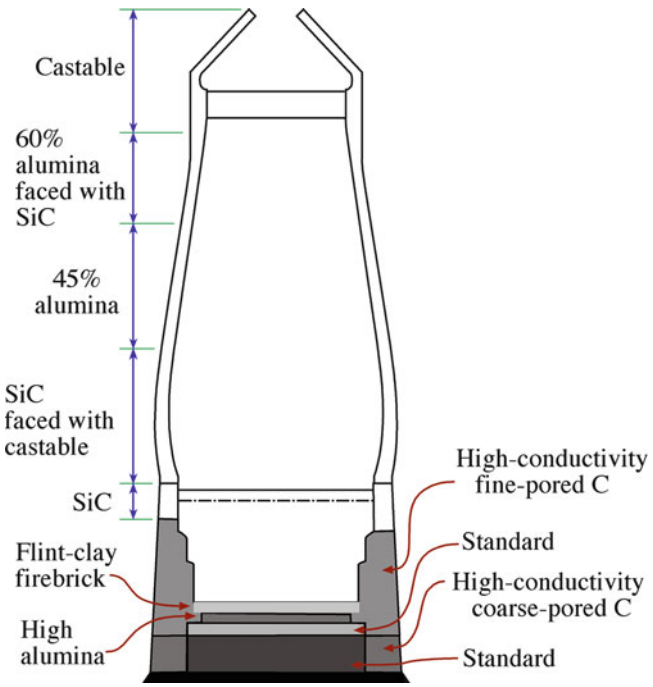

FIGURE 9.10. Diagram of a blast furnace indicating the type of refractories used in each region.

When $k_c > k_p$, the resultant thermal conductivity is

$$k_m \sim k_c[(1-V_p)/(1+V_p)] \quad (9.11)$$

As an illustration, we can use equation 9.11 to estimate the thermal conductivity of a silica firebrick containing 30 vol% porosity (i.e., $V_p = 0.3$). The values of k_c and k_p are 1.4 and 0.026 $Wm^{-1}K^{-1}$, respectively, giving a value of $k_m = 0.75$ $Wm^{-1}K^{-1}$.

Consequently, ceramics containing a high volume fraction of porosity have low values of k. The ceramic provides the high strength and high melting point requirements of the insulating material, and the porous microstructure ensures a very low k. We discuss other factors that affect thermal conductivity in Chapter 34.

In addition to their use in furnaces for ceramics processing, refractories are a very important sector of the ceramics industry because they are widely used in most high-temperature manufacturing processes.

- Iron and steel making (accounting for almost two-thirds of all refractories used)
- Copper and aluminum smelting
- Cement and ore processing
- Petroleum refining
- Petrochemical manufacturing

9.9 FURNITURE, TUBES, AND CRUCIBLES

Table 9.6 lists some of the important crucible materials. Crucibles and other furnace equipment, such as boats and setter plates, must meet the same requirements as refractory materials used for furnace insulation; that is, they must be able to withstand high temperatures and also contact with any corrosive liquids or gases used. Items such as crucibles and boats should also possess good thermal shock resistance as they may be heated and cooled rapidly. Figure 9.11 shows an example of a kiln furniture used for the production of dinnerware. Any component in contact with a crucible or other piece of furnace equipment at high temperature can be contaminated. SiO_2 is a major contaminant unless you are very careful.

9.10 FIRING PROCESS

A furnace is fired up in three stages.

- Heating-up stage
- Soaking period
- Cooling stage

The variations in the heating-up rate are chosen so that the changes of state to which the product is subject and the stresses that arise from the thermal expansion of the

TABLE 9.6 Crucible and Furnace Materials

Material	T_{max} (°C) (useful)	*Usable atmosphere*
Glasses		
Pyrex	500	ONR
Vycor	1,100	ONR
Silica glass (fused quartz)	1,200	ON(R)
Oxides		
Porcelain	1,100–1,300	ONR
Steatite, talc	1,250	ONR
Firebrick, fireclay	1,200–1,500	ONR
Firebrick, high alumina	1,600	ON(R)
Mullite ($3Al_2O_3{\cdot}2SiO_2$)	1,700	ON(R)
Sillimanite ($Al_2O_3{\cdot}SiO_2$)	1,700	ON(R)
Zircon ($ZrO_2{\cdot}SiO_2$)	1,750	ON(R)
Spinel ($MgO{\cdot}Al_2O_3$)	1,800–1,900	ONR, shock
Alumina (Al_2O_3)	1,850–1,950	ONR
Magnesia (MgO)	2,300	O, shock
Zirconia, stabilized	2,300	ON(R), shock
Thoria, stabilized	2,700	ON, shock
Metals		
Iron, nickel	1,100	(O)NR
Platinum	1,500	ONR
Rhodium	1,800	ONR
Tantalum	2,000	NR
Iridium	2,100	ONR
Molybdenum	2,100	NR
Tungsten	3,000	NR
Other		
Silicon carbide	1,500	ON
Silicon nitride	1,900	ON
Carbon, graphite	3,000	NR

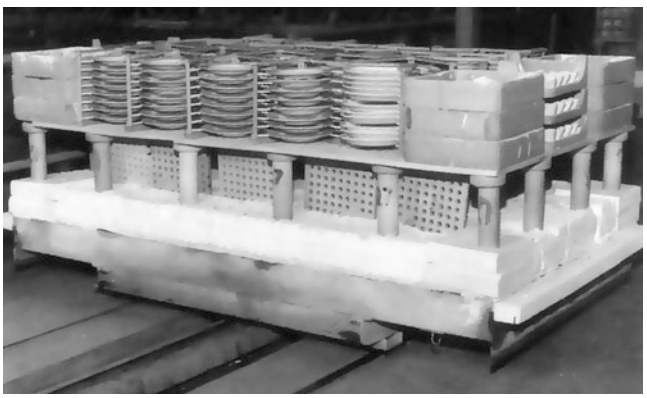

FIGURE 9.11. Kiln furniture used in the production of dinnerware.

product and the combustion of binders do not cause damage (e.g., cracks, pores). A common phase transformation that occurs during firing of silica-containing ceramics (e.g., whitewares) is that between α and β quartz at 537°C.

Furnace design and the heating mechanism determine the maximum heating rate of a furnace. It is important to always check the operating manual that came with a furnace before setting the controller.

The degree of sintering is a function of time and temperature. Different processes use different soaking

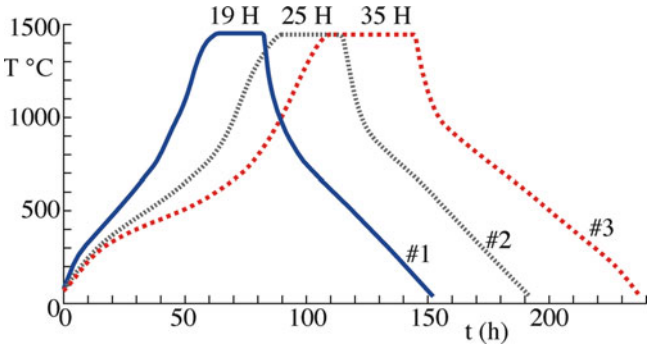

FIGURE 9.12. Firing curves for clay-bearing ceramic compositions. The soaking periods are in hours.

periods (the time at the desired firing temperature). For example, in the firing of thick-film inks, the typical soaking period is relatively short, only 6–10 min. Figure 9.12 shows examples of a much longer soaking periods used in the firing of clay-bearing ceramics.

Crystallization and other phase transformations that may occur in a product as well as thermal contraction must be taken into account in the cooling stage. At the beginning of the cooling process, the material is generally still rather plastic. It can be cooled fairly quickly at this stage because the thermal contraction does not cause the stresses to increase very much. Below a certain temperature, the plastic characteristics disappear. For many clay-based ceramics this is between 800°C and 600°C. In this range, a higher cooling rate accompanied by a steep temperature gradient can cause stresses to form in the product. In temperature ranges in which phase transformations accompanied by volume changes take place, too high a cooling rate can produce cracks. Especially when using raw materials rich in quartz, the specification of the cooling rate requires special care. One of the goals in processing both traditional and advanced ceramics is to decrease the product throughput time. Fast firing seeks to reduce total costs because of lower energy consumption and improved efficiency.

9.11 HEAT TRANSFER

The liberation of heat energy is only the first stage of the heating operation. This energy has to be transferred to the material to be heated. There are three fundamental types of heat transfer: conduction, convection, and radiation. All modes of heat transfer

- Require the existence of a temperature difference
- Are from the high-temperature medium to a lower-temperature one

A detailed study of heat transfer is best left to a specific course on this topic, or you can consult one of the standard

texts, for example Chapman (1984). Below we give a very brief description of each mode.

- Conduction is the transfer of heat from one part of a body to another part of the same body, or from one body to another that is in physical contact with it.
- Convection is the transfer of heat from one point to another within a fluid, gas, or liquid by mixing one portion of the fluid with another. In natural convection, the motion of the fluid is entirely the result of differences in density resulting from temperature.
- Radiation is the transfer of heat from one body to another not in contact with it, by means of wave motion through space.

Any, or all, of these mechanisms may be important in a particular heating application. Usually, they operate simultaneously but often with one predominating. At very high temperatures, such as those encountered in ceramic sintering, radiation is often the most important. At lower temperatures, convection is most likely to predominate.

9.12 MEASURING TEMPERATURE

In this section we describe some of the approaches used to determine the high temperatures employed in the processing of ceramics. More detailed information on temperature measurement can be found in McGee (1988).

9.12.1 Thermocouples

The most common and convenient means of measuring temperature is to use a thermocouple. The principle behind the operation of a thermocouple is the Seebeck effect, discovered in 1821 by Thomas Seebeck. If two wires of different metallic composition are connected at their ends, forming a closed circuit, an electric current flows if one of the connections is heated. Measuring the potential (electromotive force, or emf) causing this current allows the determination of temperature. In Seebeck's original research, the two metals were bismuth and copper.

There are many different types of thermocouple available to cover temperatures ranging from −273°C to 2,000°C, and the most important ones are given in Table 9.7. The type of thermocouple you would use depends mainly on the temperature range over which you require information and the desired accuracy of the temperature reading. The most commonly used thermocouples for ceramic applications are types K, R, and C. These are used for temperatures up to 1,250°C, 1,450°C, and 2,300°C, respectively. At lower temperatures it is preferable to use a base metal combination, such as chromel-alumel, which gives greater accuracy.

In furnaces, the leads of the thermocouple are usually isolated from each other and other parts of the furnace by placing them either in thin alumina sheaths or by threading alumina beads along their length. The thermocouple is ideally placed directly into the furnace cavity close to the object being heated. The external circuitry that measures temperature and, through an associated electrical circuit, controls the power to the heating elements is kept outside the furnace.

A thermocouple is a very accurate means of measuring temperature, but you should always bear in mind that the temperature being measured is that at the thermocouple tip. Unless the thermocouple is in intimate contact with the ceramic parts being heated, they may actually be at a different temperature than that measured by the

TABLE 9.7 Characteristics of Thermocouples

Type	*Combination of metals or alloys*	*Output at 900°C (mV)*	*Temperature limit °C*	*Applications*
T	Copper-constantan	20.9[a]	400	Mild oxidizing, reducing, vacuum, or inert. Good where moisture is present. Low temperature and cryogenic applications
J	Iron-constantan	21.9[a]	760	Reducing, vacuum, inert. Limited use in oxidizing at high temperatures. Not recommended for low temperatures
E	Chromel-constantan	68.8	900	Oxidizing or inert. Limited use in vacuum or reducing. Highest emf change per degree
K	Chromel-alumel	37.3	1,250	Clean, oxidizing, and inert. Limited use in vacuum or reducing. Wide temperature range. Most popular calibration
S	Pt-Pt 10%Rh	8.4	1,450	Alternative to Type K. More stable at high temps. Oxidizing or inert. Do not insert into metal tubes. Beware of contamination. High temperature
R	Pt-Pt 13%Rh	9.2	1,450	Same as type S
B	Pt 6%Rh-Pt 30%Rh	4.0	1,700	Oxidizing or inert. Do not insert into metal tubes. Beware of contamination. High temperature. Common use in glass industry
G (W)	W-W 26%Re	12.3	2,300	Vacuum, inert, hydrogen. Beware of embrittlement. Not practical below 750°C. Not for oxidizing atmosphere
C (W5)	W 5%Re-W 26%Re	16.4	2,300	Same as type G. Nonoxidizing atmosphere only
D (W3)	W 3%Re-W 25%Re	15.1	2,300	Same as type G. Nonoxidizing atmosphere only

The higher the output voltage, the simpler is the associated circuitry and/or the more accurate the temperature reading

[a]Output at 400°C

thermocouple. A good illustration of this point is that thermocouples are often used to give substrate temperatures during thin film growth. The thermocouple is frequently attached to be substrate support but is not in direct contact with the substrate itself. In controlled tests, it has been found that the measured thermocouple temperature and the actual surface temperature of the substrate can be off by as much as 100°C or in some cases even more.

9.12.2 Pyrometers

At any temperature above 0 K, all objects emit electromagnetic radiation in accordance with the Stefan-Boltzmann law:

$$E = \sigma T^4 \tag{9.12}$$

where σ is the Stefan-Boltzmann constant, which has a value of 5.6718×10^{-8} JK^{-4} m^{-2} s^{-1}. The total energy (E) emitted at all wavelengths is proportional to T^4. It is possible to estimate the temperature of a hot object by its color. In 1557, in his work on Renaissance pottery, Cipriano Piccolpasso described how the furnace operator was able to use color variations to judge furnace temperatures. As the temperature of an object increases, the range of wavelengths that it emits increases and shifts to shorter values. At temperatures above about 500°C there is red coloration that becomes increasingly orange as the temperature increases >1,000°C. At 1,400°C, the object appears bright white. Be careful when looking at hot objects, and remember that an object can still be too hot to handle even if it is not glowing red.

Optical pyrometers allow direct measurement of the temperature of an object. The disappearing filament optical pyrometer works by matching the intensity of radiant energy coming from an incandescent source to the intensity of a calibrated filament when both the source and the filament are viewed through a red filter. When the filament and the source intensities are the same, the image of the filament disappears as it is superimposed on the image of the source. An obvious requirement of this technique is that it can only be used to measure temperatures that produce visible incandescence, above about 750°C.

The advantages of the disappearing filament pyrometer are:

- The distance from the target to the source is not important (it is only necessary to have a clear image to compare with the filament image).
- Various places on a target can be examined for temperature distribution.
- Very high temperatures can be measured.
- The visible image ensures that the instrument is measuring the temperature of the desired portion of the target.
- Reasonable accuracy (at best, ±0.2°C at 775°C reduced to ±1°C at 1,225°C).

The disadvantages are:

- The instrument either must be sighted under blackbody conditions or the reading corrected for emittance.
- Absorption by dust, windows, flame, and other optical interference can produce errors.
- The disappearing filament optical pyrometer is slow and manual. However, other pyrometers such as the photoelectric optical pyrometer can be automated.

9.12.3 Pyrometric Cones

Pyrometric cones are small triangular ceramic prisms that, when set at a slight angle (known as self-supporting cones), bend over in an arc so that the tip reaches the level of the base at a particular temperature if heated at a particular rate, as shown in Figure 9.13. The bending of the cones is caused by the formation of a viscous liquid within the cone body, so that the cone bends as a result of viscous flow. The endpoint temperature when the tip of the cone touches the supporting plate is calibrated for each cone composition when heated at a standard rate. Values of endpoint temperatures for Orton cones (the U.S. name) are listed in Table 9.8 for the higher temperatures; the series actually runs from Cone 022 at 600°C, through cone 06 at 999°C to Cone 42 at the top of the scale. Because pyrometric cones are sensitive to both time and temperature, the actual temperatures associated with each

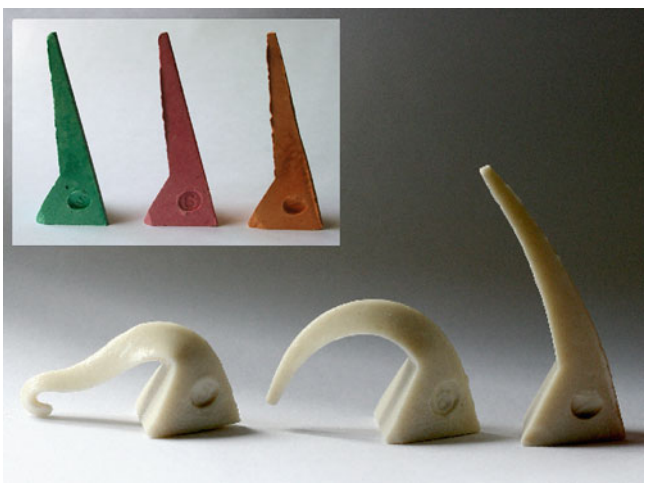

FIGURE 9.13. Orton cones: self-supporting type. The cones shown are 6 cm tall in their initial state.

TABLE 9.8 End Points of Orton Pyrometric Cones

Cone #	*Endpoint (°C)*	*Cone #*	*Endpoint (°C)*
12	1,337	31	1,679
13	1,349	$31^1/_2$	1,699
14	1,398	32	1,717
15	1,430	$32^1/_2$	1,730
16	1,491	33	1,741
17	1,512	34	1,759
18	1,522	35	1,784
19	1,541	36	1,796
20	1,564	37	1,830
23	1,590	38	1,850
26	1,605	39	1,865
27	1,627	40	1,885
28	1,638	41	1,970
29	1,645	42	2,015
30	1,654		

cone can vary, but this is also one of the reasons why they are very useful for ceramic processing. Sintering, for example, depends on both time and temperature.

9.13 SAFETY

The safety issues associated with the use of furnaces can be divided into three categories.

- *High-temperature hazards*. Working with high temperatures is the obvious safety hazard when using furnaces. Protective goggles or safety glasses should be used in all situations. As the temperature increases, the intensity of the emitted light rises, and the maximum shifts to shorter frequencies. This is apparent to an observer. At 1,000°C, the color of a furnace enclosure is a pleasing red. At 1,600°C, it is a brilliant, painful white; and goggles or glasses with green lenses should be used. Handling objects that have come from a furnace should be done using specially designed tongs and furnace tools; and hands should be protected with insulating gloves. Even if an object is not glowing red, it can still be at a temperature of >500°C.
- *Electrical hazards*. Electrical dangers should never be underestimated. All electrical equipment operating at mains voltages can be lethal. A current >100 mA (ac or dc) would almost invariably be fatal if passed through the body. Most electrical accidents are caused by worn-out equipment or faulty wiring, both of which can be avoided. All potentials in excess of a few tens of volts must be properly insulated and physically isolated before maintenance. A typical laboratory box furnace uses 240 or 208 V single phase at 50 or 60 Hz to generate 10 kW of power. This requires a current of about 40 A. All electrical equipment not fully insulated must be properly earthed in the interests of safety.
- *Chemical hazards*. Some of the chemicals used in ceramic processing are toxic. One important example is lead and its oxides, which are widely used in the production of certain types of glasses and pigments. Care should be taken to read safety data sheets that accompany any chemicals and take the necessary preventative action. Other safety issues can arise from unwanted reactions that occur within the furnace. Carbon monoxide (CO) is a deadly gas that can form from a reaction between trapped moisture (e.g., in the furnace insulation) and carbon. The source of carbon may be the graphite used in some furnaces for heating elements or in graphite-felt insulation. Problems can be avoided by ensuring that the furnace is kept dry. Domestic CO alarms can be installed in the laboratory area as an added precaution.

The importance of nitrogen ceramics, such as silicon nitride, means that furnaces are often operated using nitrogen gas. At high temperatures, it is possible to form cyanide complexes such as cyanogen (CN) and hydrogen cyanide (HCN). In graphite furnaces, the following reaction can occur

$$C + \frac{1}{2}N_2 \rightarrow CN$$

Above temperatures of 2,200°C, the CN concentration exceeds the lethal concentration guidelines. Fortunately, the gas is unstable and can be destroyed by passing it through an oxidizing flame. Hydrogen cyanide can form in graphite furnaces that contain mixtures of H_2/N_2 (called forming gas).

$$\frac{1}{2}H_2 + C + \frac{1}{2}N_2 \rightarrow HCN$$

Forming gas is used in metal sintering furnaces and in some metallization processes to avoid oxidation of the metal. HCN can also form when water vapor, graphite, and nitrogen react.

$$H_2O + 3C + N_2 \rightarrow 2HCN + CO$$

It is essential to maintain dry conditions in these furnaces, as the reaction is thermodynamically favored at all temperatures. In cases that can involve the build-up of deadly gases, it is essential that the laboratory is well ventilated, and the discharge is vented away from the immediate work area.

CHAPTER SUMMARY

Furnaces are ubiquitous in all aspects of ceramics research, development, and production. High temperatures may be obtained through harnessing the heat generated by combustion reactions, but more often it is resistance heating that is used. Ceramic materials, most notably SiC, are widely used as resistive elements in electrically heated furnaces. Ceramic materials are also used to provide thermal insulation in all types of furnace. These materials are known by the collective term refractories because of their stability at high temperatures and their resistance to corrosive environments. Refractories are a major sector of the ceramics industry, with the largest consumers being the iron and steel companies.

PEOPLE AND HISTORY

Joule, James Prescott (1818–1889) was an English physicist born in Salford near Manchester. He showed that heat is produced by motion and thus helped end the caloric theory.

Kirchhoff, Gustav Robert (1824–1887) was born in Prussia (now part of Russia) and died in Berlin. He introduced the term black-body radiation, the laws of electrical networks, and much more.

Morse, E.F. patented the disappearing filament optical pyrometer in 1899. He lived in Trumansburg, NY, up Cayuga Lake from Ithaca. Samuel Morse was connected but apparently not closely. The invention was built on Edison's 1879 idea.

Norton, Frederick Harwood formed the Ceramics Division at MIT and wrote two classic texts on ceramics.

Orton Jr., Edward J. established the first ceramic engineering program at The Ohio State University (OSU) in 1894 and founded the American Ceramic Society in 1899. He created the Standard Pyrometric Cone Company, to make pyrometric cones, in a basement at OSU; these cones became the standards for monitoring firings and are known as Orton cones (http://www.ortonceramic.com/). Similar cones may have been used in China in the Northern Song Period (before 1127 CE), although Josiah Wedgwood used pyrometric beads instead. Outside the United States similar cones may be called Seger cones (after Hermann Seger) or the Staffordshire Cones in the United Kingdom.

Seebeck, Thomas Johann (1770–1831) was born in Estonia. He showed that a current flowed when you join two metals that are at different temperatures (the thermoelectric effect). This led to the invention of the thermocouple.

EXERCISES

9.1 Table 9.4 lists materials used as furnace elements for ceramic processing. Find the costs of each type of element.

9.2 Small electrically heated box furnaces are probably the most widely used furnaces in university ceramics laboratories. What are the characteristics of these furnaces that make them so useful?

9.3 Why is a muffle furnace so named?

9.4 (a) Explain briefly why the standard molar enthalpy of combustion for ethane (C_2H_6) is greater than that for methane. (b) Which is more useful as a fuel—methane or methanol? Briefly explain how you arrived at your answer. (c) Calculate the standard molar enthalpy of combustion of methane at 1,000 K.

9.5 Explain why most refractory materials such as firebricks and fiber board insulation have high volume fractions of porosity.

9.6 Is a high thermal expansion coefficient an advantageous or deleterious property of a refractory brick? Explain briefly the reasoning behind your answer.

9.7 Briefly explain how a thermocouple works.

9.8 The most widely used thermocouples for ceramic processing are types K, R, and C. Explain what alloys are used for each type and under what conditions each would be most appropriate.

9.9 Pyrometric cones are widely used in industry for temperature measurement, yet they are rarely used in university ceramics laboratories. Why does this discrepancy exist?

9.10 Pyrex and Vycor are glasses that are used as crucibles. Why is the maximum useful temperature of Pyrex less than half that of Vycor?

9.11 Using Table 1.2, estimate the temperature of the furnace in Figure 9.1.

9.12 What type of thermocouple would be the most appropriate to measure the temperature of the furnace shown in Figure 9.1

9.13 You want a furnace that can operate at temperatures up to 1,800°C in air. Is molybdenum (Mo) a good choice for an electrical heating element for such a furnace? If not, what type of heating element would you recommend?

9.14 Name two crucible materials suitable for operation at 1,600°C in air. Compare your two choices in terms of cost.

9.15 How much does an optical pyrometer cost?

9.16 Suggest a physical reason for the changes in b in Table 9.2 and justify your answer.

9.17 Describe the current market for microwave ovens in ceramic processing, including furnaces combining microwave with other forms of heating. Document your sources and carefully critique them.

9.18 Some ceramic cups are not microwave-safe. Explain why this is so.

9.19 How do the space shuttle tiles achieve their insulation properties? Suggest how this property might be improved.

9.20 Using the library and other sources, discuss the use of a micro-electro-mechanical systems (MEMS) furnace.

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WWW

http://intarch.ac.uk/journal/issue1/peacey/toc.html introduces furnaces in archeology. It gives the definition of a muffle from *Searle, A B 1930 The Encyclopedia of the Ceramic Industries, London* as *A chamber, case or box of refractory material, which is built in a furnace, and used to heat articles out of direct contact with flames or other products of combustion. It serves a purpose similar to a saggar, but being larger, is more suitable for some purposes.* The muffle is actually the enclosed section that protects the material from the combustion products of the furnace. The heat is conducted to the sample through the walls of the muffle. www.claygirl.com/glossary.html gives other definitions for the potter