

Chapter 2

The Tradition Continued

The materials mentioned here complete the chain of ceramic materials produced since the dawn of humanity. They are mass-produced which is enabled by use of, little processed natural raw materials, having appropriate immanent properties. One can distinguish materials based on the traditions of using clay, lime and silica as well as of refractory rocks (→Fig. 1.1).

2.1 The Clay Tradition

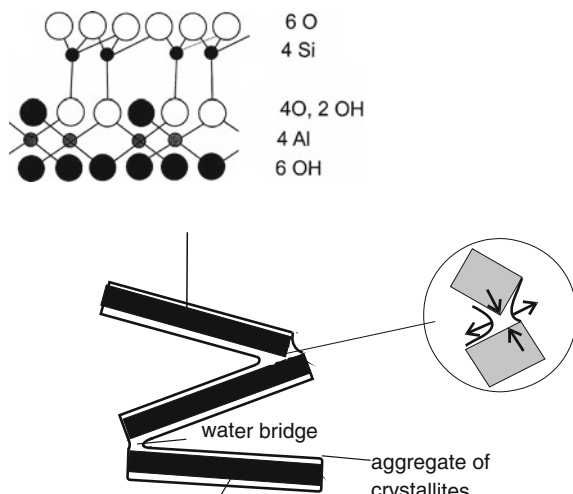
Clay-Water Mix This tradition includes products for which the basic raw material is a sedimentary rock: clay. The main components of clay are clay minerals having the structure of phyllosilicates. A typical phyllosilicate is kaolinite, $\text{Al}_4[\text{Si}_4\text{O}_{10}](\text{OH})_8$. Its atomic structure is composed of strongly bound silicon oxide and gibbsite layers (see insert in Fig. 2.1). As a result of their origin, clays contain various amounts of quartz (SiO_2) and feldspar, the most common minerals in the crust (i.e. KAlSi_3O_8 , $\text{NaAlSi}_3\text{O}_8$, $\text{CaAl}_2\text{Si}_2\text{O}_8$); and fragments of other rocks and organic substances. Kaolinite-rich clays of a low impurity contents are called kaolin.

The specific properties of clay minerals-water masses have been exploited from the beginning. Clay minerals form agglomerates composed of 2–5 crystallites with thicknesses of 2–8 nm and widths <100 nm. As a result of Coulombic attraction of hydroxide layers in crystallites and water molecules, the agglomerates are wetted by water, which forms thin layers on their surface. This results in the formation of water bridges between crystallites (Fig. 2.1). Since, the wetting angle (→Fig. 4.2 in Chap. 4) is less than 90° , the meniscus (i.e. the water-air interface) of the water bridges is concave and, due to the low thickness of the water layers, has a very small radius of curvature.

There is a relationship between the chemical potential of atoms and surface curvature:

$$\Delta\mu = \gamma\Omega\left(\frac{1}{a_1} + \frac{1}{a_2}\right) \quad (2.1)$$

Fig. 2.1 Agglomerate of clay minerals crystallites with adsorbed water layers. *Top* insert: cell of kaolinite structure; *right* insert: capillary forces in water bridges between the crystallites



where: $\Delta\mu$ —the chemical potential difference of atoms on curved and flat surfaces; γ —surface tension at the interface (here at the water-air interface); Ω —atomic volume; a_1 and a_2 —two basic curvature radii, whereby $a_i > 0$ for a convex surface and $a_i < 0$ for a concave surface. According to Eq. (2.1), atoms on the convex side have higher and on the concave side lower chemical potential than on a flat surface. A chemical potential gradient is therefore formed across the interface. Since $\text{grad}(\mu) = -F$, where F is force, forces, called capillary, arise at the interface. For water surface tension $\gamma = 7.2 \cdot 10^{-2} \text{ [N} \cdot \text{m}^{-1}]$ and a_1 equal to several nm, the capillary force can be as high as $1 \cdot 10^3 \text{ Pa}$.

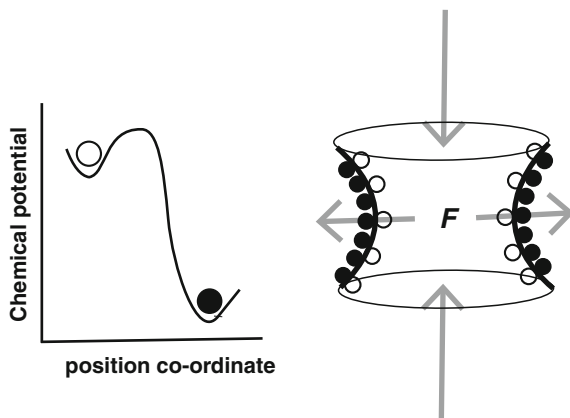
In equilibrium, the capillary forces in the water bridges are balanced by identical compressive forces acting perpendicularly to them (Fig. 2.2). This causes agglomerates of clay mineral crystallites to be strongly attracted to one another.

To lower the resulting cohesion of crystallites more water must be added and to initiate deformation of the clay in this state stress has to be applied. On increasing the applied stress above a limit value (plasticity limit) the ‘lubricating’ action of water facilitates a further increase in deformation. After the load is relieved, the capillary forces cause the clay-water mix to retain the deformation from the load. This is referred to as plastic behaviour.

Deformation of material by shearing requires, as a rule, the application of a lower stress than for other modes of applying load. Such a deformation can be achieved at many points of the clay-water mix, if tangent stress is applied to its surface. The discovery of this behaviour of the clay-water mix is believed to have been the reason behind an innovation introduced around 5,000 years ago in Sumer, namely, the formation of clay products with a potter’s wheel.

Slurries Agglomerates of clay minerals’ crystallites can be, under some conditions, permanently dispersed in water, forming suspensions, also referred to as slips or slurries. There is an evidence for the stabilisation of slurries through the use of

Fig. 2.2 Chemical potential of atoms at the convex and concave sides of a liquid-gas interface (*left-hand schema*) and compressive forces due to capillary forces in the water bridges (*right-hand schema*)



alkali-rich plant ash as early as the Hellenistic era, i.e. around 2,300 years ago. We know now that this is due to positive influence of K^+ or Na^+ present in the water solution. The durability of slurry is, namely, explained by sorption of these alkaline cations onto negatively charged sites in clay minerals' crystallites. Achieving in this way identical positive surface charges, the crystallite agglomerates repel one another, preventing their flocculation. However, the effect of cations being surrounded with a hydration layer competes with the tendency of their direct sorption. Today it is known that the effectiveness of K^+ or Na^+ results from their tendency to become surrounded with thin hydration layers only. With insignificant concentrations, e.g. between 10^{-2} and 10^{-4} M, of potassium or sodium cations in the water solution, a double electric layer is formed around the crystallite aggregates (Fig. 2.3a). A certain number of cations of this layer are strongly bound to the aggregate surface; the remaining part of that layer, however, can easily move under the shear load. Stable slurries can also be created by adsorbing on the surface of the aggregates organic molecules which form steric hindrances against an approach of the aggregates (Fig. 2.3b).

Phase Transformations During Firing The finds from the peak of development of the Neolithic revolution bear witness to, discovery at this time that the clay-water mix, when fired at temperatures achievable when burning wood, turns into a solid and strong body. We know now more about the transformations which occur in kaolinite-feldspar—quartz mixes during firing (Fig. 2.4). This knowledge permits to conclude that a decisive role in formation of the strong body plays a highly viscous SiO_2 and Al_2O_3 -rich liquid appearing about $800^\circ C$. Wetting solid particles, the liquid forms bridges between them (Fig. 2.5) and on this way capillary forces are aroused (\rightarrow Fig. 2.2) owing to which the system is in a state corresponding to application of external hydrostatic compressive stress. The stress is considered to be the driving force of sintering, i.e. increase of packing density and cohesion of the particles at elevated temperature. The action of the SiO_2 - and Al_2O_3 -rich liquid is very effective in sintering, as testified by a high strength of the porous body of

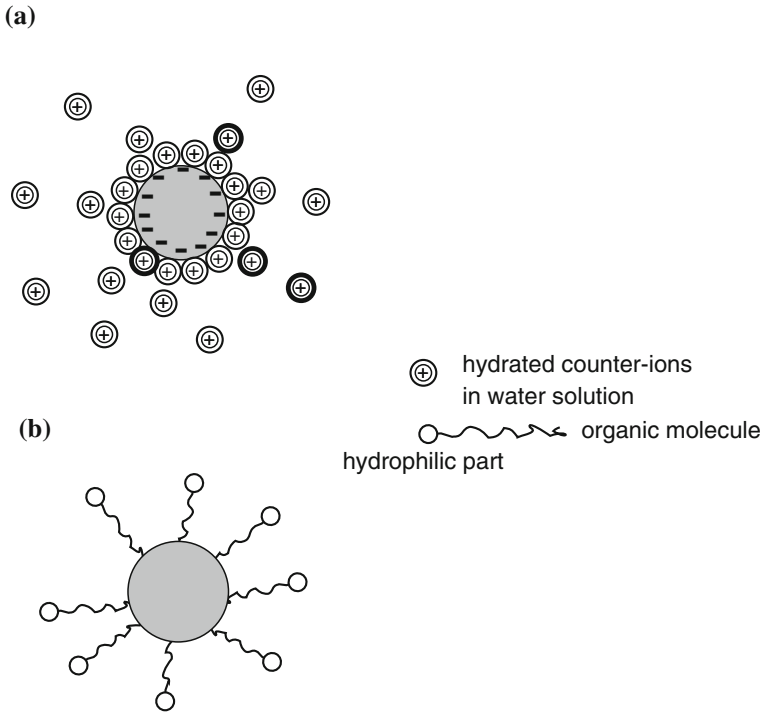


Fig. 2.3 Stabilisation of suspensions of solid particles in water: creation of a double layer by sorption of hydrated anti-ions (a); creation of steric hindrances by sorption of organic chain molecules with hydrophobic and hydrophilic functional groups (b)

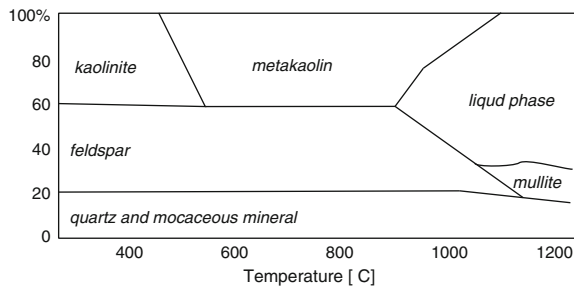


Fig. 2.4 Phase transformations during firing of: kaolinite $[\text{Al}_4[\text{Si}_4\text{O}_{10}](\text{OH})_9]$ —feldspars $[\text{K,Na} \text{AlSi}_3\text{O}_8\text{-CaAl}_2\text{Si}_3\text{O}_8\text{-}]$ quartz $[\text{SiO}_2]$ mixses (generalised)

earthenware. A less porous microstructure is obtained by using a higher percentage of K and Na-containing feldspars in the mix and higher temperature of firing. Both factors increase the amount of the liquid phase formed on firing and its viscosity. Owing to this the liquid nearly completely fills up the pores. In this way, the

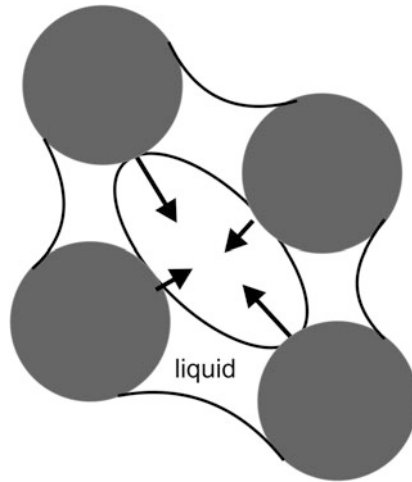


Fig. 2.5 Porous system of solid particles wetted by a liquid at an elevated temperature. Due to capillary forces arising in liquid bridges between the particles, the system is in a state corresponding application of an external hydrostatic compressive stress which is the driving force. For sintering increasing the packing density of particles with elimination of pores

microstructure of porcelain body is formed, which is dense and impermeable to water and gases, and transparent in thin-walled products. Because relatively pure raw materials, like kaolin, are used—the porcelain body is more or less white. Most of the liquid phase solidifies on cooling as brittle glassy phase (→next section) but this is compensated by an enhanced crystallisation of secondary mullite (composition close to $\text{Al}_6\text{Si}_2\text{O}_{13}$). Secondary mullite crystallises in form of needles of a high strength, and their grid reinforces the brittle glassy phase.

The composition of raw materials mixes used to obtain the mentioned products and stoneware, composed of still more glassy phase than porcelain, is shown in Fig. 2.6.

2.2 The Silica Tradition

Oxide Glass The formation of melts solidifying into a vitreous, amorphous phase on cooling down has been discovered already in ancient times. Mixtures of solid components, containing, as we know today, around 70 % SiO_2 and 30 % $\text{Na}_2\text{O} + \text{CaO}$, were molten at temperatures achievable when burning wood to obtain upon cooling a transparent material: glass. The chemical composition of today's standard oxide glass, such as [silica] soda-lime glass, does not differ significantly from that of antique glass (Table 2.1). However, for special applications, other

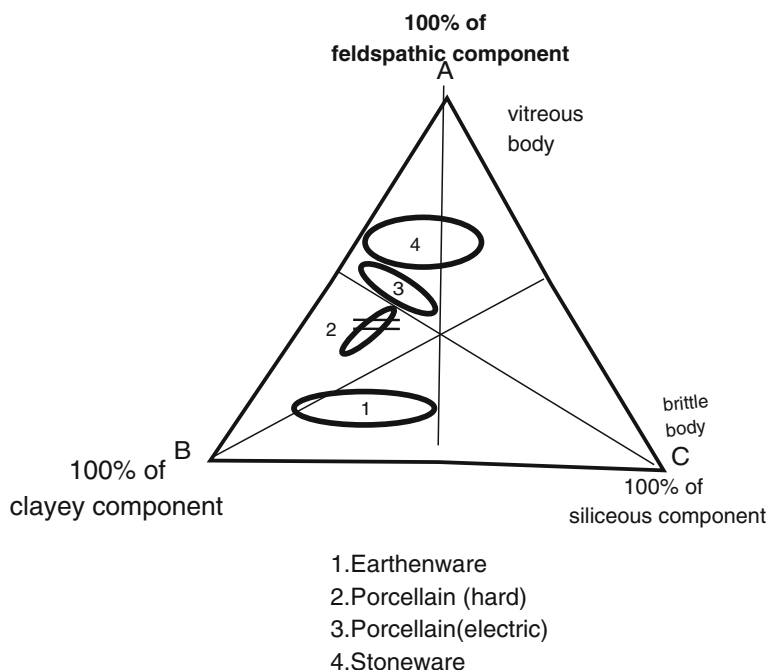


Fig. 2.6 Typical compositions used for production of earthenware, porcelain and stoneware

Table 2.1 Composition of antique and modern window and pottery glass types

	SiO ₂	Al ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	B ₂ O ₃
Babylonian glass (fifteenth to fourteenth century BC)	64	1	6	6	5	18	
Egyptian glass (fourteenth to eleventh century BC)	66	1	6	5	3	19	
Modern window and pottery glass	73–74	0–1	9–10	1	1	15	<1

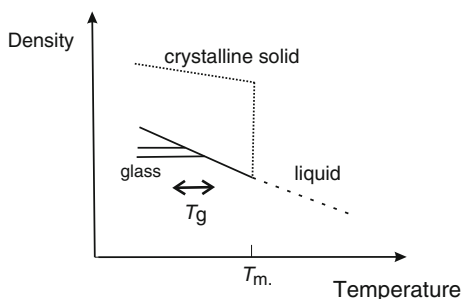
types of oxide glass have developed over time. These include borosilicate glass, in which the addition of a small amount of alkalis to SiO₂ and B₂O₃ makes it possible to obtain products with a thermal expansion coefficient ($\alpha = 3\text{--}6 \cdot 10^{-6} \text{ }^\circ\text{C}^{-1}$) lower than that of soda-lime glass ($\alpha = 1 \cdot 10^{-5} \text{ }^\circ\text{C}^{-1}$) and with greater resistance to an aggressive environment. Furthermore, lead glass which contains SiO₂ and PbO, along with small shares of sodium and potassium, is characterised by a high gloss and can be formed into various shapes within a wider temperature range. These properties are used, for example, to manufacture decorative glass products ('crystal' glass), as well as in electronics. The oxide glass family also includes aluminosilicate glass (called E or S glass), which includes an increased proportion of Al₂O₃, MgO

and CaO. Such glass is characterised by mechanical properties superior to those of most other glass types (Fig. 2.7).

Non-oxide Glass The tendency to form amorphous solids like the oxide glasses is not limited to oxygenous systems. It also occurs when oxygen is replaced with fluorine and, at the same time, Si, Ge or B are replaced or supplemented by other elements. In this way are obtained, for example, fluoride glasses, containing 57 % molar ZrF_4 , 36 % BF_3 , 4 % LaF_3 and 3 % AlF_3). Chalcogenide glass, containing e.g. molar percentages of 48 % Te, 30 % As, 12 % Si and 10 % Ge, have specific properties which distinguish them from oxide glass. Namely, a high-crystallisation rate which may be initiated by a laser pulse within only 30 or so nanoseconds and very good transparency to infrared radiation (wavelength range from 0.6 to 15 μm). The electrical conductivity and reflectance (\rightarrow 5. Materials versus light) of the crystalline and amorphous chalcogenide differ significantly. Through appropriate heating and cooling cycles, point sequences can be created with stronger and weaker light reflection, corresponding, respectively, to bits = 1 and = 0 in the binary mathematical system. This makes it possible to save and read binary information on CD-ROMs and DVDs.

Glass Structure Glass formation has been better, if only phenomenologically, understood now than in ancient times. In the case of liquid metal alloys and ionic substances, a first-order transformation usually occurs while cooling at a relatively low rate. At a specific temperature it causes transition of the liquid into the thermodynamically more stable crystalline phase. In oxide liquids which can be transformed into glass (typical are liquids containing around 70 % SiO_2 and 30 % $\text{Na}_2\text{O} + \text{CaO}$), the first-order transformation does not occur. However, at a temperature referred to as the glass point, a second-order transformation is observed, during which the liquid gradually passes to a solid with an amorphous structure, presumably inherited to a considerable degree from the liquid. Although in the absence of direct methods it is difficult to speak of details, the lack of x-ray diffraction in glass proves that, in contrast to crystalline structures, there is no

Fig. 2.7 Density changes at on a first-order liquid-crystalline solid phase transition and on attaining the glass point by a liquid



T_g - glass-forming temperature
 T_m - melting point

long-range order in glass, but at most short-range order. The possible atomic structure of crystalline and amorphous silicon dioxide is illustrated in Fig. 2.8, assuming that it is formed in both cases by tetrahedral $[\text{SiO}_4]$ groups, bound together by common oxygen atoms, called oxygen bridges. While there is short-range order in the tetrahedral groups, their network in amorphous form of SiO_2 lacks long-range order (Fig. 2.8b).

The amorphous network can be modified by Al^{3+} and Ti^{4+} , and by Ca^{2+} , Li^+ , Na^+ , K^+ . Three probable types of reactions of the cations, introduced in form of oxides, with the silicon-oxygen network are: oxygen donation to the silicon-oxygen network causing breaking of the oxygen bridges (Fig. 2.9a); oxygen donation increasing the number of oxygen atoms coordinated with the central silicon atom (Fig. 2.9b); a combination of both reactions (Fig. 2.9c). The type of reaction may be assumed to depend on the cation-oxygen Coulombic attraction, which is proportional to the ratio of the cationic charge to its radius, z/r . For Si^{4+} coordinating 4 anions of oxygen, $z/r = 1.6 \cdot 10^{-8} [\text{C} \cdot \text{m}^{-1}]$, which contrasts with $z/r = 0.1 \cdot 10^{-8} [\text{C} \cdot \text{m}^{-1}]$ in the case of K^+ and Na^+ and $z/r = 0.3 \cdot 10^{-8} [\text{C} \cdot \text{m}^{-1}]$ at Ca^{2+} , Mg^{2+} and Li^+ . Therefore, it can be assumed that when introducing potassium oxides or sodium to the silicon-oxygen melt, the reaction illustrated in Fig. 2.9a dominates.

TTT Graphs These and other considerations, however, are more or less speculative so it is worth to keep on the phenomenological aspects of glass formation. To this end, a TTT (time-temperature-transformation) graph will be used (Fig. 2.10). The shadowed area in Fig. 2.10 corresponds to time-temperature conditions in which more than a 1 % of the liquid is crystallising when a melt is cooled from a higher temperature. Therefore, a liquid at initial temperature T_p will not be crystallising as long as it is cooled at a higher rate than minimum, given by:

$$dT/dt_{\min} \approx (T_p - T_{\min})/t_{\min} \quad (2.2)$$

Fig. 2.8 Two-dimensional schema of a crystalline structure **a** and amorphous network in glass **b** composed of $[\text{SiO}_4]$ tetrahedral coordination groups

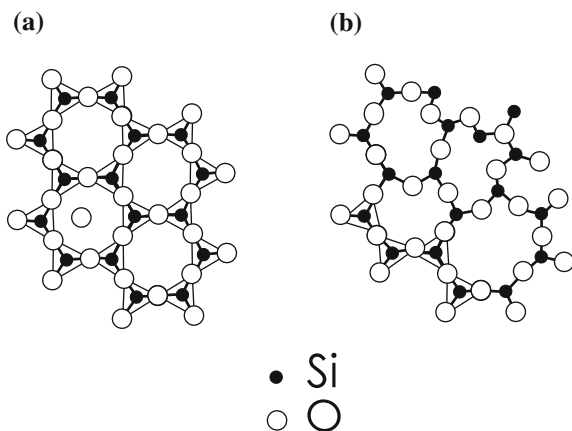


Fig. 2.9 Probable reactions of oxides with amorphous silicon-oxygen network.

a Donation of oxygen to the silicate network resulting in breaking down of oxygenbridges in the network. **b** Donation of oxygen to the silicate network resulting in an increased number of oxygen atoms coordinated with silicon. **c** Combination of reactions **a** and **b**

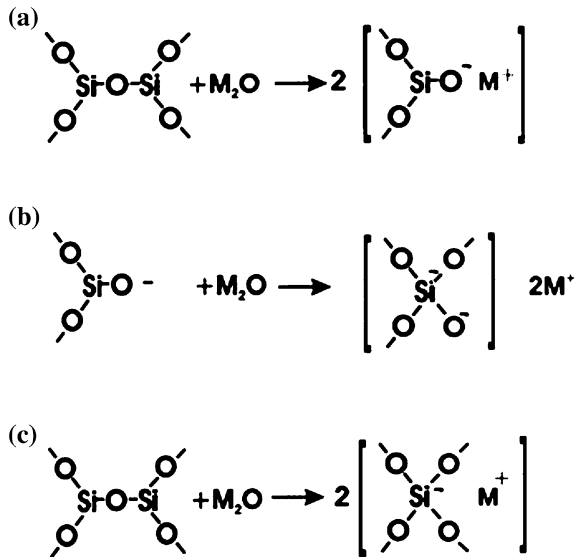
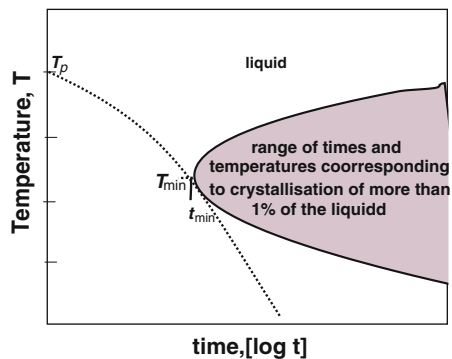


Fig. 2.10 Temperature-time-transformation (TTT) graph, typical for a soda-lime glass composition. The application the TTT graph is explained in the text



Minimum Cooling Rates for Glass Formation where: T_p initial temperature of the liquid; the temperature; the values of T_{\min} and time t_{\min} —are Indicated on the graph. The minimum cooling rate corresponds to the dotted line in Fig. 2.10. Table 2.2 specifies the minimum cooling rates determined experimentally for various systems. These constitute a measure of the tendency of various liquids to making glass while being cooled. In contrast to many silicon-oxygenous system, to produce metallic glass, extremely high cooling rate is necessary.

Devitrificates Glass products with specific properties include devitrificates. They are typically composed of a 30–90 % volume of small crystalline grains of ceramic phases bonded with non-transformed glass. Generally speaking, devitrificates have the characteristics of both crystalline and amorphous phases, which can be changed over a broad range. Compared to glass, the presence of crystalline phases in

Table 2.2 Approximate minimum cooling rates for liquids required to create an amorphous vitreous phase

Substance	dT/dt [$^{\circ}\text{C}\cdot\text{s}^{-1}$]
Soda-lime glass	$1\cdot 10^{-5}$
SiO_2	$1\cdot 10^{-4}$
As_2S_3	$1\cdot 10^{-1}$
metals	1.108

devitrificates reduces, for example, the value of the thermal expansion coefficient and thus increases resistance to thermal shocks (see further text on refractory tradition) while also increasing mechanical strength and resistance to brittle fracture.

The formation of ceramic crystalline phases in devitrificates, ceramisation, is performed through controlled crystallisation of a heated glassy mass. The continuous network typical for glass has to be modified to allow the formation and growth of the crystalline phase. In case of silicate glasses one method is to introduce suitable network-modifier cations to the liquid which, by initiating the reactions illustrated in Fig. 2.9, causes the Si-O-Si bonds to break and smaller silicon-oxygen domains to form. This, in turn, causes increased mobility of domains, which promotes the crystallisation. An important role is also played by the presence of interfaces. At interfaces, the potential energy barrier for crystallisation is lower than in the bulk and (heterogeneous) nucleation is facilitated. These requirements are met only by some systems, for example, those shown in Table 2.3.

Glaze An amorphous silicon-oxygen vitreous phase is the main constituents of the t matrix of glazes. The term glaze is used to describe vitreous layers applied to the porous ceramic body to strengthen, waterproof and decorate it. Accordingly, their properties of the vitreous layers have in first place to be adjusted to the body, so that the glaze and ceramic body form a coherent, mechanically and thermally resistant structure. This applies in particular to adjusting the thermal expansion coefficient,

Table 2.3 Some three- and four-component systems used for the fabrication of devitrificates and the crystalline phase in devitrificates

System	Crystalline phase	
$\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$	Anorthite	$\text{CaAl}_2\text{Si}_2\text{O}_8$
$\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$	Cordierite	$\text{Mg}_3\text{Al}_4\text{Si}_5\text{O}_{18}$
	Spinel	MgAl_2O_4
$\text{MgO-CaO-Al}_2\text{O}_3\text{-SiO}_2$	Anorthite	$\text{CaAl}_2\text{Si}_2\text{O}_8$
	Cordierite	$\text{Mg}_3\text{Al}_4\text{Si}_5\text{O}_{18}$
	Spinel	MgAl_2O_4
	Diopside	$\text{CaMgSi}_2\text{O}_6$
$\text{ZnO-Al}_2\text{O}_3\text{-SiO}_2$	Gahnite	ZnAl_2O_4
	Willemite	Zn_2SiO_4
$\text{Li}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$	Spodumene	$\text{LiAlSi}_2\text{O}_6$
	Eucryptite	LiAlSiO_4

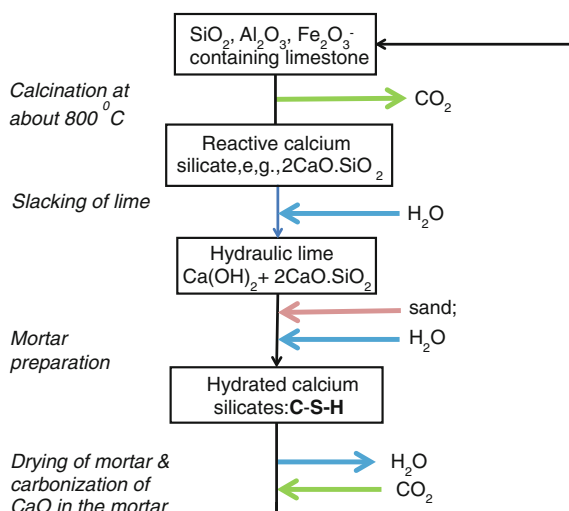
which enables reduction of residual thermal stress (\rightarrow 3. Ceramics to overcome brittleness) at the body-glaze interface. Recent developments include a transformation of the amorphous glaze into polycrystalline devitrificates (see previous text) which makes it more mechanically strong and resistant to thermal shocks, and making TiO_2 -rich glazes, to activate photocatalysis in which light photons generate bactericidal radicals (\rightarrow 1. A brief history of ceramic innovation). Other issues, related to the optical properties of glazes, shall be discussed in more detail in an appropriate context (\rightarrow 6. Materials versus light).

2.3 The Lime Tradition

Properties of Ca–O Groups The term used here refers to the fact that calcium compounds, such as the gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), quicklime (CaO), or calcium silicates that form the bulk of Portland cement clinker, have played a key role in the field of construction materials. The latter include mortars for bonding building construction blocks and the blocks themselves, followed by decorative moulding, drywall panels for partition walls, ceilings a.s.o. The use of, gypsum and sand mortars was reported as early as in ancient Egyptian times, and quicklime mortars were used on a wider scale not only in the Roman Empire, but also in earlier structures in Minoan Crete.

These applications result from specific properties of Ca–O groups, namely, their high reactivity with CO_2 and water. Reactivity with CO_2 is used to obtain non-hydraulic lime mortars in a cycle of reactions shown in Fig. 2.11. Natural limestone is converted to reactive quicklime(CaO) which, when mixed with water, forms, after some time, a thick slurry that can be applied on construction blocks to bond

Fig. 2.11 Cycle of reactions used in the case of non-hydraulic lime mortars



them together; the slurry, reacting with CO_2 from the atmosphere, turns back into a layer of limestone of moderate strength.

Portland Cement The most widespread material exploiting the unique properties of calcium compounds has been, for over 150 years, hydraulic Portland cement, which sets after mixing with water and binds a mineral aggregate. Therefore, it can be used to make concrete, which became an indispensable construction material for the foundations of buildings and dams, and an important material in road, bridge and building construction. A wide variety of concrete types have been created for different applications. Let us mention three of them. Standard concrete is a mixture of hydraulic cement, fine and/or coarse mineral aggregate and possibly some other additives (up to 5 %). At some point after mixing with water and compacting with vibrating equipment, durable concrete is formed. At the end of the twentieth century, self-compacting concrete was developed—a mixture of cement, aggregate and various chemicals with high initial liquidity which, when cast in any shape, compacts itself under its own weight. Another product is cellular concrete, made by subjecting the mix to steam which causes the simultaneous formation of a large number of pores and setting of cement.

The intermediate product in the production of concrete is so-called Portland cement clinker, a clinker made by firing marl (clay, containing calcium carbonate and quartz sand) at a temperature of about $1,450^\circ\text{C}$. The typical phase composition of the clinker is shown in Table 2.4. The cement used to form a water suspension (cement paste) also contains gypsum to slow down the hydration and setting processes, thus preventing significant internal stress and cracking of the solidified hydration product. Moreover, high-strength cement contains typically small additions of silica dust to reduce the crystallisation of calcium hydroxide in the hydration product.

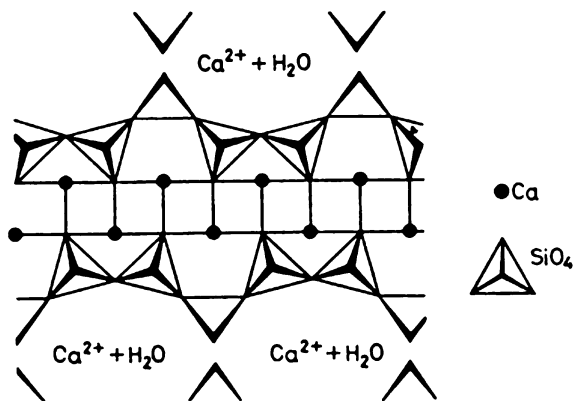
The hydration mechanism was phenomenologically investigated mainly for alite ($3\text{CaO}\cdot\text{SiO}_2$, C_3S), which forms 55–75 % of Portland cement clinker. This process depends on the growth of a water-insoluble hydration product, which is calcium silicate hydrate, or C-S-H (the so-called tobermorite-like or jennite-like phase). The growth involves successive addition to two-dimensional silicon-oxygen chains, with a cross-section diameter of several nanometres, of $[\text{SiO}_4]$ coordination tetrahedra, Ca^{2+} ions and H_2O molecules (Fig. 2.12). The reasons for the growth of such fibrous phases are not clear and the explanations are controversial. More understandable are

Table 2.4 Typical phase composition of Portland cement clinker^a

Phase	Percentage
$3\text{CaO}\cdot 2\text{SiO}_2$ (C_3S , alite)	55–75
$2\text{CaO}\cdot\text{SiO}_2$ (C_2S , belite)	<25
$3\text{CaO}\cdot\text{Al}_2\text{O}_3$ (C_3A)	<12
$4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_2$ (C_3AF)	<8

^a In addition to ground clinker, the Portland cement contains ca 3.5 % $\text{CaSO}_4\cdot\text{H}_2\text{O}$ to slow down the reaction of C_3A with water

Fig. 2.12 Structure of tobermorite- and jennite-phases formed during hydration of alite (schematic)



the results: the hardening of the alite-water systems due to growth of the two-dimensional tobermorite- and jennite-like phase in the water space. The fibrous matter branches off, forming a tangled net, the branching probably due to the internal stress caused by defects. Given the considerable surface area, the cohesion of these fibrous matters should be substantial, which would reasonably explain the great strength (particularly compressive) of the hydration product. This product also contains numerous pores with radii of ca 2 nm and less frequent voids with larger diameters. In classic cement, about 10 % of its volume consists of Ca(OH)₂ particles larger than 1 μm as well as particles of aluminosilicate phases. To some degree, these particles compensate for the effect of the fibrous net formation, hence the addition of silica dust in high-strength Portland cement products.

Refractory Cements There are also other types of hydraulic cements. An example is a cement produced since the mid-twentieth century whose main ingredients are the calcium aluminates CaO·Al₂O₃ (CA) and 2 CaO·7Al₂O₃. These compounds react exothermically with water. An increase in temperature due to the reaction causes the rapid dissolution of anhydrous aluminates in water and the subsequent precipitation of hydrated aluminates from the supersaturated solution in form of a tangled net. This results, at first, in the formation of a thick paste, and then of a solid with significant strength. In addition to a high setting (hardening) rate, such cements are characterised by high resistance to high temperatures. Therefore, they are increasingly used as refractory compounds for the lining of high-temperature equipment, and are often called refractory cements.

In the twenty-first century, attention has been drawn to materials, hardening within several minutes at a temperature about 100 °C. However, this is but based on a different mechanism than in the case of lime, Portland cement or refractory cements. These are so-called geopolymers, which constitute a category of inorganic polymers, with the nominal composition $y\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot \text{M}_2\text{O}$ (M = Na, K or Cs, $3 < y < 35$). Their structure is formed most probably of nanocrystallites with a zeolite-like structure (→Fig. 4.6), composed of [SiO₄] and [AlO₄] coordination polyhedra, bonded together via oxygen bridges. The positive charge of Al³⁺,

smaller than that of Si, is compensated by the presence of alkaline cations, such as K, Na or Li.

The precursors of the geopolymers are mostly waste pozzolanic materials, which include metakaolin (\rightarrow Fig. 2.4), volatile ash and blast furnace slag. They ensure the rapid and easy dissolution of SiO_2 and Al_2O_3 in highly alkaline water solutions, e.g. in hydroxide $\text{Na}(\text{OH})$ or sodium metasilicate Na_2SiO_3 —so-called water glass. As a result sols are created in which monomer hydroxides of the Si-O-Al-O -[poly(silalane)], -Si-O-Al-O-Si-O -[poly(silalane-siloxide)] type are found. Those monomers are polycondensed at moderate temperatures (up to 100°C) according to the reaction: $\text{R-OH} + \text{-HO-R} = \text{R-O-R} + \text{H}_2\text{O}$.

The driving force of geopolymer applications is environmental protection. First, waste material is used to produce them. Secondly, it is important that considerably less CO_2 is released into the atmosphere during their production than in the case of Portland cement. The properties of solidified products of geopolymers are also important. While the properties of Portland cement deteriorate rapidly if the temperature is increased to about 400°C , the mechanical strength of the products of geopolymer setting is retained up to $800\text{--}1,200^\circ\text{C}$, owing to their transformation into thermally resistant aluminosilicates such as nepheline $\text{KNa}_3[\text{AlSiO}_4]_4$, calcsilite $\text{K}[\text{AlSiO}_4]$, leucite ($\text{K}[\text{AlSi}_2\text{O}_6]$) and pollucite $\text{Cs}[\text{AlSi}_2\text{O}_6]$.

2.4 The Refractory Tradition

Microstructure and Properties Producing and handling molten and hot metals, melting of glass-forming compositions, Portland cement clinker and coke production waste incineration all require constructions (furnaces, kilns, ovens) clad with refractories, i.e. materials that can withstand temperatures from $1,200$ to $1,500^\circ\text{C}$. Although bloomery-type furnaces (pits dug in clay) had been used for centuries, the mass production of refractories started only during the Industrial Revolution. Because of great market demand (\rightarrow Table 1.1), both early and contemporary refractory materials have been made mainly of low-modified natural raw materials. Due to the high operating temperatures of refractory materials, these include substances whose mineral ingredients are melting above $1,700^\circ\text{C}$ (SiO_2), $2,000^\circ\text{C}$ ($\alpha\text{Al}_2\text{O}_3$) or $2,500^\circ\text{C}$ (Cr_2O_3 , MgO , CaO). They are used in the form of pastes or components made by pressure-forming and sintering at a high temperature. With raw materials comminuted to particles of $<1\text{ mm}$, a total porosity of 40 % can be achieved and further reduced by compressing. On heating the pulverised raw materials, liquid eutectics are formed due to the presence of silica-rich impurities, and liquid bridges created between the solid grains. In a way shown in Fig. 2.5 the contact area and cohesion of grains are increased to a higher level, sufficient for refractory materials performance under their own weight. The chemical composition and the porous microstructure permit to achieve:

1. retention of their form and integrity under their own weight at temperatures up to 1,500 °C (or even higher);
2. resistance to high-temperature corrosion in aggressive environment (liquids, gases and slag);
3. low thermal conductivity; which ensures thermal insulation of the hot interior of high-temperature furnaces and reactors;
4. resistance to sudden temperature changes (thermal shocks), to which many refractory linings are subjected.

High-Temperature Corrosion Let us make more detailed comments. High-temperature corrosion is mainly due to reactions between refractory materials and the aggressive environment. In addition to reactions with aggressive gases, these are mainly reactions with molten metals, glass and particularly with slag floating on the surface of melted metal or glass. Such reactions may cause transformations in the material with loss of weight and deterioration of properties.

In the case of refractory materials made of oxide ingredients, the reactions are mainly an acid-base ones; in materials based on SiC and Si₃N₄, oxidation-reduction reactions also take place. In general, the intensity and rate of the acid-base reactions is highest when one of the substances involved is acidic and the other basic. The rate decreases when the acidity or basicity of the substances is similar. This is illustrated in the example in Table 2.5, in which shown is the dissolution rate of an acidic refractory material in a molten basic FeO.

Magnesite (based on MgO), chromium-magnesite (based on Cr₂O₃ and MgO), dolomite (based on (Ca,Mg) O), baddeleyite (based on ZrO₂) and graphite refractories are alkaline. Therefore, they are suitable for applications where the aggressive liquid, slag or atmosphere is alkaline. This is true of furnaces for melting iron and non-ferrous metals, of continuous steel casting equipment and of kilns for production of Portland cement clinker. When an aggressive liquid, slag or atmosphere is acidic, such as a molten glass compositions, acidic materials are used. These include silica (based on SiO₂), aluminosilicate (e.g. based on fireclays or mullite) refractories. Where there are both acidic and alkaline ingredients in the slag and amphoteric is the atmosphere, neutral refractory materials, such as corundum (based on Al₂O₃) or chromite (Cr₂O₃), are used successfully.

Carbide and nitride refractories (based on SiC, Si₃N₄, B₄C or BN) are used mainly for handling hot solid non-ferrous metals (e.g. copper) and in coal-burning furnaces or in waste incinerators. Burning coal at high temperatures produces

Table 2.5 Solubility rate in a basic liquid (FeO)

Material (ranged according to decreasing acidity)	Solubility rate [mg·cm ⁻² ·s ⁻¹]
SiO ₂	40.0
Al ₂ O ₃	8.5
MgO	9.4
Refractory chromo-magnesite	4.4

highly aggressive molten alkaline salts and silicates to which resistant are only the carbide- and nitride-based materials. Waste incineration requires (unless a complex system of filters is used) a temperature so high that it can be handled only by the carbide and nitride refractories.

High resistance to thermal shocks and low-thermal conductivity are both ensured by a relatively high porosity of the refractories (Fig. 2.13).

Thermal Stress Sudden temperature changes of the ambient (thermal shocks) cause an inhomogeneous temperature distribution and thus thermal stress in materials. These stresses, especially tensile ones, can bring about brittle fracture. A simple model, shown in Fig. 2.14, will be used to explain this. A very thin plate (with negligible thickness in direction z) is a model of external layers of a hot material, which become cold due to a sudden temperature decrease in the ambient. For a non-zero thermal expansion coefficient α of the material, the plate dimensions tend to decrease on cooling. The model plate, like the external layers of a material, is fixed in direction x to a rigid substrate which is a model of the bulk of the material which does not initially change its temperature and dimensions.

Let us now conduct a mental experiment, in the first stage of which the plate, cooled from T_p to T , freely adapts its dimension to temperature changes in the ambient, so that it shrinks in direction y and x (direction z can be omitted because

Fig. 2.13 Properties of refractory materials versus porosity. *Note* The properties of non-porous materials serve as a reference point, equal to 100 %

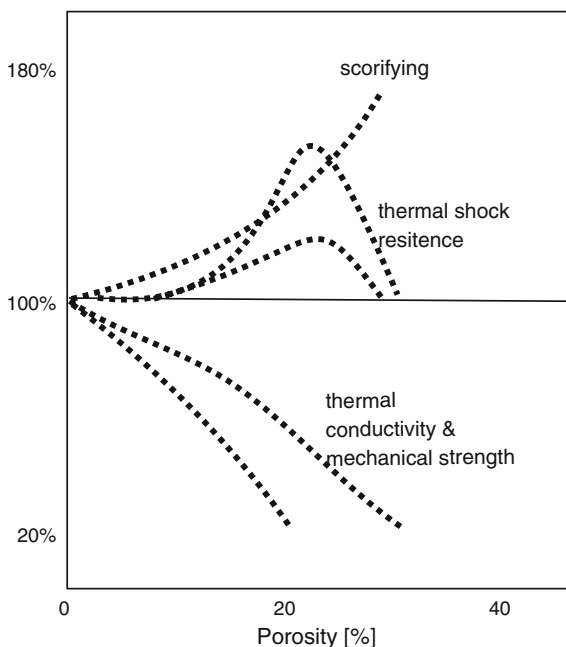
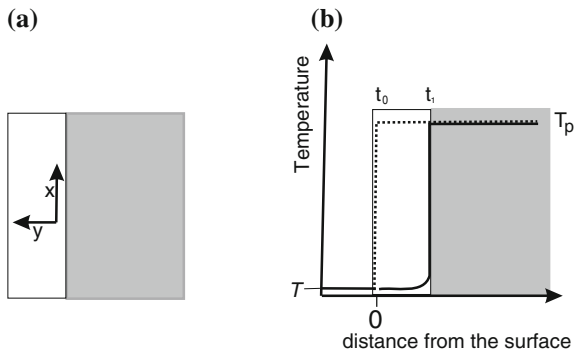


Fig. 2.14 A thin plate rigidly fixed to the substrate which does not change its size with temperature (a).

Temperature distribution in the hot model (dotted line) and immediately after placing it in a cool environment of a temperature T (continuous line) (b)



of the low thickness of the plate). The relative strain in the directions x and y , $\varepsilon_x < 0$, is specified approximately by:

$$\varepsilon_x = \varepsilon_y = \bar{\alpha}(T - T_p) \quad (2.3)$$

where: $\bar{\alpha}$ —average linear thermal expansion coefficient for the material of the plate. In fact, the plate can freely change its size in direction y only but not in direction x , because it is rigidly fixed to the substrate. To restore the actual condition, the freely shrunk plate has to be expanded by $\varepsilon_x > 0$, by applying tensile stress $\sigma_x > 0$. Assuming that on sudden dimensional changes the behaviour of the plate is elastic ($\sigma_x = E\varepsilon_x$, where E is the Young's modulus), the Eq. (2.3) can be re-written as:

$$\sigma_x = -E\varepsilon_x = E\bar{\alpha}_x(T_p - T) = E\bar{\alpha}AT \quad (2.4)$$

The thermally induced stress thus increase with ΔT and at a certain value of ΔT crack propagation can start in the material, reducing the strength of material. It can be assumed that refractory materials, working under the weight of the lining only, can retain their integrity up to 20 % of their original strength. The value of ΔT at which the strength is reduced to this point can be taken as a measure of the material resistance to thermal shocks, ΔT_{\max} . As shown in Fig. 2.15, the strength reduction due to thermal stress brought about by sudden temperature changes may take place suddenly or stepwise. The former case is typical for monolithic materials where a once initiated crack propagation continues through the whole material at a speed of sound (Fig. 2.16a). The gradual decrease of mechanical strength due to thermal stresses, found with porous materials, can be attributed to a presence of grain boundaries with various mechanical strength in the porous material. Decohesion occurs locally, first at the weakest interfaces (Fig. 2.16b). As the weak grain boundaries are statistically distributed, a net of separated small cracks is formed in the material which decreases the strength stepwise.

Thermal Conductivity The influence of porosity on thermal conductivity λ [$\text{J} \cdot \text{s}^{-1} \cdot \text{m}^{-1} \cdot \text{deg}^{-1}$] shall be discussed by using the mathematical model presented in

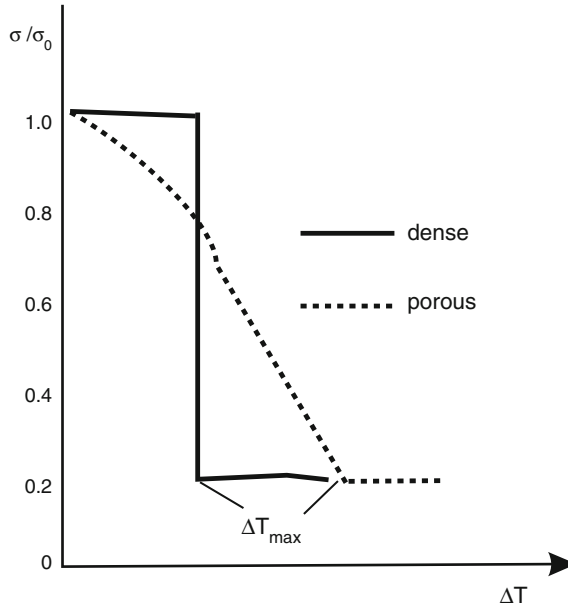


Fig. 2.15 Ratio of bending strength after σ and before σ_0 a sudden drop of temperature by ΔT for a dense and a porous material. The maximum temperature difference which the materials can sustain, ΔT_{\max} , corresponds here to ΔT at which the ratio decreases to $\sigma/\sigma_0 = 0.2$. Typical values of ΔT_{\max} range from 200 °C (glass) and 800 °C (porous SiC)

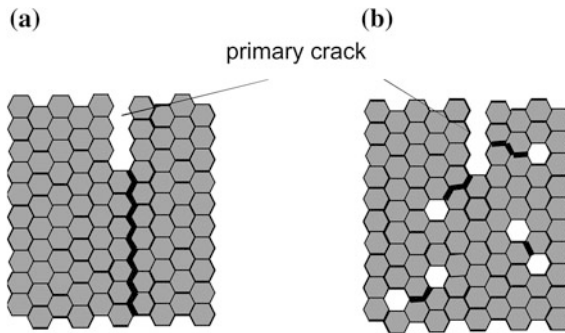


Fig. 2.16 Cracking due to thermal stress: Of a material with homogeneous microstructure **a** and of a porous material with varied mechanical strength of grain boundaries **(b)**

Fig. 2.17. Thermal energy q [J] transported through the model is the sum of energy transported via the phase 1 and 2, respectively:

$$q = q_1 + q_2 \quad (2.5)$$

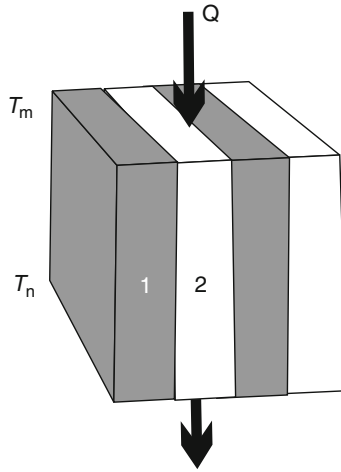


Fig. 2.17 Mathematical model of two-phase materials; phases (marked with indices 1 and 2). In the model: there is a stationary flow of heat (Q) between the surface at temperature T_m and the surface at temperature $T_n < T_m$. $T_m - T_n$ and the temperature gradient are thus equal for both phases

Given the dimension of λ , Eq. (2.5) can be—written as:

$$\lambda(V\Delta Tt/L^2) = \lambda_1(V_1\Delta Tt/L^2) + \lambda_2(V_2\Delta Tt/L^2) \quad (2.6)$$

where the lower indices 1 and 2 stand for the phase 1 and phase 2; V for volume; L for thickness; ΔT for temperature gradient; t —for time. As L , ΔT and $t = \text{const}$, Eq. (2.6) can be rewritten:

$$\lambda V = \lambda_1 V_1 + \lambda_2 V_2 \quad (2.7)$$

Introducing the notion of volume fraction of a phase $V'_i = V_i/V$ ($i = 1, 2$), Eq. (2.7) yields:

$$\lambda = \lambda_1 V'_1 + \lambda_2 V'_2 \quad (2.8)$$

Let us assume that index 1 denotes a solid l with better thermal conductivity and index 2 a gaseous phase (contained in the pores) with much lower conductivity $\lambda_2 \ll \lambda_1$. In this case:

$$\lambda = \lambda_1 V'_1 = \lambda_1 (1 - V'_2) \quad (2.9)$$

In other words, heat is conducted mainly by the superior heat conductor 1 (solid), thermal conductivity decreasing linearly with volume fraction of the inferior heat conductor 2, i.e. pores containing gas. Except for fibrous materials, Eq. (2.9) works well for volume fractions of pores up to 20 %.

As shown in Fig. 2.13, mechanical strength of refractory materials decreases along with the volume fraction of pores. In practice, refractory materials perform only under their own weight. Therefore, strength reduction with porosity is less important than the increase of material resistance to thermal shocks and decrease of thermal conductivity accompanying an increased porosity. It must be noted, however, that with higher porosity there is a higher infiltration of the refractory material by an aggressive liquid phase, and considerable infiltration of slag may reduce the life of refractory material. The discussion shows that requirements for refractory materials are often contradictory. Therefore, their phase composition and microstructure are usually a result of compromise based on experience.

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