CHAPTER 13

APPLICATIONS AND PROCESSING OF CERAMICS

PROBLEM SOLUTIONS

Glasses

Glass-Ceramics

13.1 Two desirable characteristics of glasses are optical transparency and ease of fabrication.

13.2 (a) Crystallization is the process whereby a glass material is caused to transform to a crystalline solid, usually by a heat treatment.

(b) Two properties that may be improved by crystallization are (1) a lower coefficient of thermal expansion, and (2) higher strengths.

Refractories

13.3 For refractory ceramic materials, three characteristics that improve with increasing porosity are (1) decreased thermal expansion and contraction upon thermal cycling, (2) improved thermal insulation, and (3) improved resistance to thermal shock. Two characteristics that are adversely affected are (1) load-bearing capacity and (2) resistance to attack by corrosive materials.

13.4 (a) From Figure 12.25, for a spinel-bonded magnesia material (88.5 wt%MgO-11.5 wt% Al_2O_3), the maximum temperature without a liquid phase corresponds to the temperature at the MgO(ss)-[MgO(ss) + Liquid] boundary at this composition, which is approximately 2220°C (4030°F).

(b) The maximum temperature without the formation of a liquid phase for a magnesia-alumina spinel (25 wt%MgO-75 wt% Al_2O_3) lies at the phase boundary between $MgAl_2O_4$(ss)-($MgAl_2O_4$ + Liquid) phase fields (just slightly to the right of the congruent melting point at which the two phase boundaries become tangent); this temperature is approximately 2070°C (3760°F).

13.5 For each section of this problem two SiO_2-Al_2O_3 compositions are given; we are to decide, on the basis of the SiO_2-Al_2O_3 phase diagram (Figure 12.27), which is the more desirable refractory and then justify the choice.

(a) The 99.8 wt% SiO_2-0.2 wt% Al_2O_3 will be more desirable because the liquidus temperature will be greater for this composition; therefore, at any temperature within the cristobalite + liquid region on the phase diagram, there will be a lower fraction of the liquid phase present than for the 99.0 wt% SiO_2-1.0 wt% Al_2O_3 composition, and, thus, the mechanical integrity will be greater.

(b) The 74 wt% Al_2O_3-26 wt% SiO_2 composition will be more desirable because, for this composition, a liquid phase does not form until about 1750°C [i.e., the temperature at which a vertical line at 74 wt% Al_2O_3 crosses the boundary between the mullite and (mullite + liquid) phase regions]; for the 70 wt% Al_2O_3-30 wt% SiO_2 material, a liquid phase forms at a much lower temperature--1587°C.

(c) The 95 wt% Al_2O_3-5 wt% SiO_2 composition will be more desirable because the liquidus temperature will be greater for this composition. Therefore, at any temperature within the alumina + liquid region on the phase diagram, there will be a lower fraction of the liquid phase present than for the 90 wt% Al_2O_3-10 wt% SiO_2 composition, and, thus, the mechanical integrity of the 95 wt% Al_2O_3-5 wt% SiO_2 material will be greater.

13.6 This problem calls for us to compute the mass fractions of liquid for two fireclay refractory materials at 1600°C. In order to solve this problem it is necessary that we use the SiO_2-Al_2O_3 phase diagram (Figure 12.27). The mass fraction of liquid, W_L, as determined using the lever rule and tie line at 1600°C, is just

$$W_L = \frac{C_{\text{mullite}} - C_0}{C_{\text{mullite}} - C_L}$$

where C_{mullite} = 72 wt% Al_2O_3 and C_L = 8 wt% Al_2O_3, as determined using the tie-line; also, C_0 is the composition (in weight percent Al_2O_3) of the refractory material.

(a) For the 25 wt% Al_2O_3-75 wt% SiO_2 composition, C_0 = 25 wt% Al_2O_3, and

$$W_L = \frac{72 - 25}{72 - 8} = 0.73$$

(b) For the 45 wt% Al_2O_3-55 wt% SiO_2 composition, C_0 = 45 wt% Al_2O_3, and

$$W_L = \frac{72 - 45}{72 - 8} = 0.42$$

13.7 This problem asks that we specify, for the MgO-Al_2O_3 system, Figure 12.25, the maximum temperature without the formation of a liquid phase; it is approximately 2800°C which is possible for pure MgO.

Cements

13.8 For clay-based aggregates, a liquid phase forms during firing, which infiltrates the pores between the unmelted particles; upon cooling, this liquid becomes a glass, that serves as the bonding phase.

With cements, the bonding process is a chemical, hydration reaction between the water that has been added and the various cement constituents. The cement particles are bonded together by reactions that occur at the particle surfaces.

Fabrication and Processing of Glasses and Glass-Ceramics

13.9 We are asked to compute the weight of soda ash and limestone that must be added to 125 lb_m of SiO_2 to yield a glass composition of 78 wt% SiO_2, 17 wt% Na_2O, and 5 wt% CaO. Let x = the weight of Na_2O and y = the weight of CaO. Then, employment of a modified form Equation 4.3, we may write the following expressions for the concentrations of Na_2O (C_{Na_2O}) and CaO (C_{CaO}):

$$C_{Na_2O} = 17 \text{ wt\%} = \frac{x}{125 + x + y} \times 100$$

$$C_{CaO} = 5 \text{ wt\%} = \frac{y}{125 + x + y} \times 100$$

Solving for x and y from these two expressions yields x = 27.2 lb_m Na_2O and y = 8.0 lb_m CaO.

Now, in order to compute the weights of Na_2CO_3 and $CaCO_3$, we must employ molecular weights. The molecular weights of Na_2CO_3 $\left(MW_{Na_2CO_3}\right)$ and Na_2O $\left(MW_{Na_2O}\right)$ are as follows:

$$MW_{Na_2CO_3} = 2(A_{Na}) + A_C + 3(A_O)$$

$$= 2(22.99 \text{ g/mol}) + 12.01 \text{ g/mol} + 3(16.00\text{g/mol}) = 105.99 \text{ g/mol}$$

$$MW_{Na_2O} = 2(A_{Na}) + A_O$$

$$= 2(22.99 \text{ g/mol}) + 16.00 \text{ g/mol} = 61.98 \text{ g/mol}$$

And, finally, the mass of Na_2CO_3 $\left(m_{Na_2CO_3}\right)$ is equal to

$$m_{Na_2CO_3} = (27.2 \text{ lb}_\text{m})\left(\frac{MW_{Na_2CO_3}}{MW_{Na_2O}}\right)$$

$$= (27.2 \text{ lb}_\text{m})\left(\frac{105.99 \text{ g/mol}}{61.98 \text{ g/mol}}\right) = 46.5 \text{ lb}_\text{m}$$

Likewise, the molecular weights of $CaCO_3$ $\left(MW_{CaCO_3}\right)$ and CaO $\left(MW_{CaO}\right)$ are as follows:

$$MW_{CaCO_3} = A_{Ca} + A_C + 3(A_O)$$

$$= 40.08\text{ g/mol} + 12.01\text{ g/mol} + (3)(16.00\text{ g/mol}) = 100.09\text{ g/mol}$$

$$MW_{CaO} = A_{Ca} + A_O$$

$$= 40.08\text{ g/mol} + 16.00\text{ g/mol} = 56.08\text{ g/mol}$$

Such that the mass of $CaCO_3$ $\left(m_{CaCO_3}\right)$ is equal to

$$m_{CaCO_3} = (8.0\text{ lb}_m)\left(\frac{MW_{CaCO_3}}{MW_{CaO}}\right)$$

$$= (8.0\text{ lb}_m)\left(\frac{100.09\text{ g/mol}}{56.08\text{ g/mol}}\right) = 14.3\text{ lb}_m$$

13.10 The glass transition temperature is, for a noncrystalline ceramic, that temperature at which there is a change of slope for the specific volume versus temperature curve (Figure 13.6).

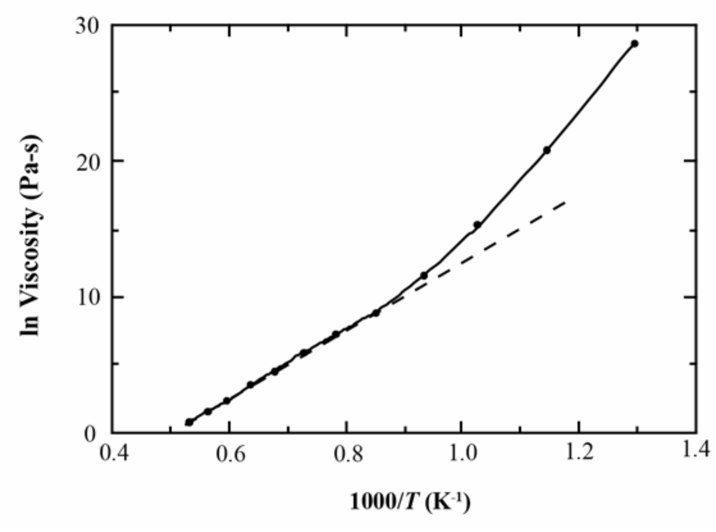
The melting temperature is, for a crystalline material, that temperature at which there is a sudden and discontinuous decrease in the specific-volume-versus-temperature curve.

13.11 The annealing point is that temperature at which the viscosity of the glass is 10^{12} Pa-s (10^{13} P). From Figure 13.7, these temperatures for the several glasses are as follows:

Glass	Annealing Temperature
Soda-lime	500°C (930°F)
Borosilicate	570°C (1060°F)
96% Silica	930°C (1705°F)
Fused silica	1170°C (2140°F)

13.12 The softening point of a glass is that temperature at which the viscosity is 4 x 10^6 Pa-s; from Figure 13.7, these temperatures for the 96% silica, borosilicate, and soda-lime glasses are 1540°C (2800°F), 830°C (1525°F), and 700°C (1290°F), respectively.

13.13 (a) Below is shown the logarithm viscosity versus reciprocal of temperature plot for the soda-lime glass, using the data in Figure 13.7. The dashed line has been drawn through the data points corresponding to temperatures between 900 and 1600ºC (as stipulated in the problem statement).



(b) The activation energy, Q_{vis}, may be computed according to

$$Q_{vis} = R\left[\frac{\Delta \ln \eta}{\Delta\left(\frac{1}{T}\right)}\right] = R\left(\frac{\ln \eta_1 - \ln \eta_2}{\frac{1}{T_1} - \frac{1}{T_2}}\right)$$

where R is the gas constant, and $\frac{\Delta \ln \eta}{\Delta\left(\frac{1}{T}\right)}$ is the slope of the dashed line that has been constructed. Taking $1/T_1$ and $1/T_2$ as 0.6 x 10^{-3} and 1.10 x 10^{-3} K^{-1}, respectively, then the corresponding values of ln η_1 and ln η_2 are 2.5 and 15.0. Therefore,

$$Q_{vis} = R\left(\frac{\ln \eta_1 - \ln \eta_2}{\frac{1}{T_1} - \frac{1}{T_2}}\right) = (8.31 \text{ J/mol} - \text{K})\left(\frac{2.5 - 15.0}{0.6 \text{ x } 10^{-3} \text{K}^{-1} - 1.10 \text{ x } 10^{-3} \text{ K}^{-1}}\right)$$

$$= 208{,}000 \text{ J/mol}$$

13.14 This problem calls for us to determine the maximum temperature to which a cylindrical specimen of borosilicate glass may be heated in order that its deformation be less than 2.5 mm over a week's time. According to Equation 6.1

$$\sigma = \frac{F}{A_0} = \frac{2 \text{ N}}{\pi\left(\frac{4 \text{ x } 10^{-3} \text{ m}}{2}\right)^2} = 1.59 \text{ x } 10^5 \text{ Pa}$$

Also,

$$\frac{d\varepsilon}{dt} = \frac{d\left(\frac{\Delta l}{l_0}\right)}{dt}$$

$$= \frac{2.5 \text{ mm}/125 \text{ mm}}{(1 \text{ wk})(7 \text{ days}/\text{week})(24 \text{ h}/\text{day})(3600 \text{ s}/\text{h})} = 3.31 \text{ x } 10^{-8} \text{ s}^{-1}$$

Thus,

$$\eta = \frac{\sigma}{d\varepsilon/dt} = \frac{1.59 \text{ x } 10^5 \text{ Pa}}{3.31 \text{ x } 10^{-8} \text{ s}^{-1}} = 4.8 \text{ x } 10^{12} \text{ Pa - s}$$

From Figure 13.7, the temperature at which the viscosity of the borosilicate glass is 4.8 x 10^{12} Pa-s is about 540°C (1005°F).

13.15 (a) Residual thermal stresses are introduced into a glass piece when it is cooled because surface and interior regions cool at different rates, and, therefore, contract different amounts; since the material will experience very little, if any deformation, stresses are established.

(b) Yes, thermal stresses will be introduced because of thermal expansion upon heating for the same reason as for thermal contraction upon cooling.

13.16 Borosilicate glasses and fused silica are resistant to thermal shock because they have relatively low coefficients of thermal expansion; therefore, upon heating or cooling, the difference in the degree of expansion or contraction across a cross-section of a ware that is constructed from these materials will be relatively low.

13.17 Thermal tempering of glasses is described in Section 13.9.

13.18 Chemical tempering will be accomplished by substitution, for Na^+, another monovalent cation with a slightly larger diameter. From Table 12.3, both K^+ and Cs^+ fill these criteria, having ionic radii of 0.138 and 0.170 nm, respectively, which are larger than the ionic radius of Na^+ (0.102 nm). In fact, soda-lime glasses are tempered by a K^+-Na^+ ion exchange.

Fabrication and Processing of Clay Products

13.19 Two desirable characteristics of clay minerals relative to fabrication processes are (1) they become hydroplastic (and therefore formable) when mixed with water; and (2) during firing, clays melt over a range of temperatures, which allows some fusion and bonding of the ware without complete melting and a loss of mechanical integrity and shape.

13.20 Clays become hydroplastic when water is added because the water molecules occupy regions between the layered molecular sheets; these water molecules essentially eliminate the secondary molecular bonds between adjacent sheets, and also form a thin film around the clay particles. The net result is that the clay particles are relatively free to move past one another, which is manifested as the hydroplasticity phenomenon.

13.21 (a) The three components of a whiteware ceramic are clay, quartz, and a flux.

(b) With regard to the role that each component plays:

Quartz acts as a filler material.

Clay facilitates the forming operation since, when mixed with water, the mass may be made to become either hydroplastic or form a slip. Also, since clays melt over a range of temperatures, the shape of the piece being fired will be maintained.

The flux facilitates the formation of a glass having a relatively low melting temperature.

13.22 (a) It is important to control the rate of drying inasmuch as if the rate of drying is too rapid, there will be nonuniform shrinkage between surface and interior regions, such that warping and/or cracking of the ceramic ware may result.

(b) Three factors that affect the rate of drying are temperature, humidity, and rate of air flow. The rate of drying is enhanced by increasing both the temperature and rate of air flow, and by decreasing the humidity of the air.

13.23 The reason that drying shrinkage is greater for products having smaller clay particles is because there is more particle surface area, and, consequently, more water will surround a given volume of particles. The drying shrinkage will thus be greater as this water is removed, and as the interparticle separation decreases.

13.24 (a) Three factors that influence the degree to which vitrification occurs in clay-based ceramic wares are: (1) composition (especially the concentration of flux present); (2) the temperature of firing; and (3) the time at the firing temperature.

(b) Density will increase with degree of vitrification since the total remaining pore volume decreases.

Firing distortion will increase with degree of vitrification since more liquid phase will be present at the firing temperature.

Strength will also increase with degree of vitrification inasmuch as more of the liquid phase forms, which fills in a greater fraction of pore volume. Upon cooling, the liquid forms a glass matrix of relatively high strength.

Corrosion resistance normally increases also, especially at service temperatures below that at which the glass phase begins to soften. The rate of corrosion is dependent on the amount of surface area exposed to the corrosive medium; hence, decreasing the total surface area by filling in some of the surface pores, diminishes the corrosion rate.

Thermal conductivity will increase with degree of vitrification. The glass phase has a higher conductivity than the pores that it has filled.

Powder Pressing

13.25 The principal disadvantage of hot-isostatic pressing is that it is expensive. The pressure is applied on a pre-formed green piece by a gas. Thus, the process is slow, and the equipment required to supply the gas and withstand the elevated temperature and pressure is costly.

DESIGN PROBLEM

13.D1 (a) Important characteristics that are required of a ceramic material to be used for kitchen cookware are: (1) it must have a high resistance to thermal shock (Section 19.5) in order to withstand relatively rapid changes in temperature; (2) it must have a relatively high thermal conductivity; 3) it must be relatively strong and tough in order to endure normal kitchen use; and 4) it must be nontoxic.

(b) Possible materials worth considering are a common soda-lime glass, a borosilicate (Pyrex) glass, and a glass ceramic. These materials and some of their characteristics are discussed in this chapter. Using Equation 17.9 a comparison of the resistance to thermal shock may be made. The student will need to obtain cost information.

(c) It is left to the student to make this determination and justify the decision.