6. Silicate ceramics

6.0 Introduction

The main types of silicate ceramics are based either on alumosilicates (→ kaolin- or clay-based ceramic such as porcelain, earthenware, stoneware and bricks; system K₂O-Al₂O₃-SiO₂) or on magnesium silicates (→ talc-based technical ceramics such as steatite, cordierite and forsterite ceramics; system MgO-Al₂O₃-SiO₂). Special groups are zircon- and mullite-based fine ceramics (for electrical insulators) as well as low-thermal expansion ceramics in the system Li₂O-Al₂O₃-SiO₂ (for thermoshock-resistant tableware), which have an extremely narrow sintering interval and are therefore preferentially produced by glass-ceramic techniques (i.e. devitrification of glasses by nucleation and growth). Silicate ceramics are conventionally subdivided into coarse or fine and, according to water absorption, into dense (< 2 % for fine and < 6 % for coarse) or porous ceramics (> 2% and > 6 %, respectively).

6.1 Kaolin- and clay-based ceramics and dental porcelain

In the ternary raw material diagram (kaolin/clay–feldspar–quartz) the composition of all kaolin- and clay-based ceramics lies in the mullite field, that of dental porcelain in the leucite field.

- **Main types of dense silicate fine ceramics:**
  - Hard porcelain (the majority of middle-European porcelains – common firing temperatures approx. 1400 ± 50 °C).
  - Soft porcelain (e.g. old Asian and “vitreous china“, firing temperature 1200–1300 °C, higher content of fluxes).
  - Bone china (English, based on up to 50 % bone ash as a raw material – apart from kaolin, quartz), frit porcelain (French, based on glass frits, 1150 °C) and “parian“ (unglazed ornamental porcelain with a low kaolin content of < 40 %).
  - Dental porcelain (feldspar content approx. 80 %, kaolin < 5 %, firing temperature < 1250 °C).
  - Electrotechnical porcelain for insulators; usually containing alumina (instead of quartz in earlier types of electrotechnical porcelain) in order to increase the mechanical and electrical strength (firing temperature approx. 1250 °C).

- **Hard porcelain:**
  - Porcelain is a densely sintered (defined by a water absorption < 2 %), white and translucent fine ceramic material prepared from natural raw materials; typical raw material mixture for hard porcelain: 50 % kaolin (part of which can be replaced by plastic clay), 25 % quartz and 25 % feldspar (preferentially K-feldspar).
  - Hard porcelain: after firing at 1400 ± 50 °C (with a relatively broad sintering interval) the final ceramic body consists of min. 50 % glass phase, max. 25 % mullite and max. 25 % residual quartz (which can be partly transformed to cristobalite); typical properties: density 2.3–2.5 g/cm³, tensile modulus 70–80 GPa, Poisson ratio 0.17, flexural strength up to 100 MPa, thermal conductivity 1.2–1.6 W/mK, thermal expansion coefficient 4–6·10⁻⁶ K⁻¹.
At temperatures < 1100 °C the clay minerals (mainly kaolinite) dehydrate (→ metakaolinite above 500–600 °C) and form transient phases by releasing silica (→ defective spinel phase above 900–1000 °C), quartz undergoes polymorphic transitions and mixed K-Na-feldspars (perthites) may homogenize; at temperatures > 1100 °C: formation of feldspar melt causing liquid phase sintering (vitrification), partial dissolution of quartz (→ viscosity increase) and formation of mullite, either directly from the clay minerals (primary mullite) or by reaction of the clay minerals with the feldspar melt (secondary mullite).

- **Other types of kaolin- and clay-based silicate ceramics:**
  - **Earthenware:** porous, non-transparent fine ceramics with a white or colored body; typically fired at 1200 ± 50 °C and glazed with a PbO-containing glaze in a second firing cycle (at approx. 1100 °C); typical raw material compositions are 50–55 % clay, 40 ± 5 % quartz and 5–10 % feldspar; commonly used for tableware and tiles (for the latter, however, firing is a single-step process at about 1100 °C); “faience” is earthenware with a white body, “majolika” with a colored body, “terracotta” is coarse earthenware.
  - **Stoneware:** porous, non-transparent coarse ceramics with a colored body, typically fired at 1250 ± 50 °C (for sanitary ware, floor tiles and sewer pipes with a brown NaCl glaze); note, however, that another variant of stoneware (for tableware, tiles and chemical vessels) is a dense fine ceramic (vitrified stoneware); sanitary ware is between porcelain and stoneware.
  - **Bricks:** porous coarse ceramics, produced from cheap, local clays and loams, typically fired at 900–1000 °C; the loams should not contain pyrite and sulfates → CaSO₄ near the body surface (→ hydration → volume expansion), neither calcite (CaCO₃) → may remain unreacted as free CaO after firing (→ hydration → volume expansion); important properties: frost resistance (requires low porosity) and thermal insulation (requires high porosity).

### 6.2 Talc-based technical ceramics

All talc-based technical ceramics (ternary phase diagram MgO-Al₂O₃-SiO₂) require precise firing control (narrow sintering interval of a few °C).

- **Steatite ceramics:** basic raw materials – talc and clay (+ feldspar or BaCO₃); desired phase – protoenstatite in approx. 30 % glassy matrix; firing temperature 1350–1370 °C; problem to be controlled: transformation of the high-temperature proto- into (low-temperature) clinoenstatite, accompanied with volume expansion.
- **Cordierite ceramics:** basic raw materials – talc, clay and Al₂O₃; desired phase – cordierite in a glassy matrix; self-glazing effect by non-wetting melt exuded onto the surface; low thermal expansion coefficient (2·10⁻⁶ K⁻¹). Note that only silica glass and Li₂O-Al₂O₃-SiO₂ (glass-) ceramics exhibit lower thermal expansion coefficients (< 0.5·10⁻⁶ K⁻¹) → higher thermal shock resistance.
- **Forsterite ceramics:** basic raw materials – talc and clay (+ MgCO₃); firing is less sensitive with respect to temperature (since at 1360 °C only a small amount of eutectic melt is formed and this amount does not change very much with temperature), but very sensitive to changes in composition; high thermal expansion coefficient (11·10⁻⁶ K⁻¹) enables welding with metals (→ vacuum electrotechnics).
**Complex exercise problem:** Use the ternary phase diagrams of the systems $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ and $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ to discuss the phase composition of hard porcelain, cordierite ceramics, forsterite ceramics and steatite ceramics. *Additional explicit questions:*

a.) What are the essential high-temperature reactions for transforming the raw material mixtures into the final phase composition of these ceramic products after firing?

b.) Which microstructural features contradict the prediction from the equilibrium phase diagrams and what are the reasons for the occurrence of non-equilibrium phases?