Ceramic Industries

Part 1:
Raw Materials and Reactions

Reference:
Shreve's Book, Chapter 9 (pp. 149 – 155)

Introduction

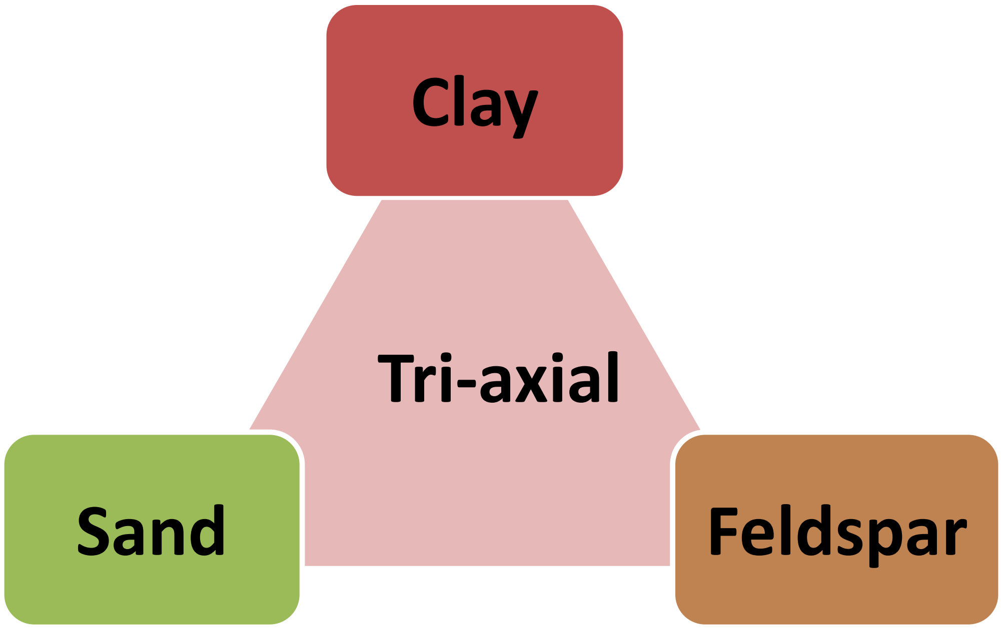
- **Ceramic Industries** (also referred to as ***clay products*** or ***silicate industries***) are providing markets with a variety of products that are essentially ***silicates***.
- Ceramic products are known to withstand high temperature, resist high pressures, have superior mechanical properties, posses special electric characteristics, and can protect against corrosion.

Introduction

❑ Examples of ceramic products are:

- **Whitewares** (pottery, porcelain, stoneware, etc.)
- **Structural Clay Products** (Building brick, sewer pipes, etc.)
- **Refractories** (Firebricks, silicon carbide refractories, etc.)
- **Glasses**
- **Enamels and enameled metals**
- **Ceramic composites**
- **Abrasives**

Basic Raw Materials of Ceramics



Some additives can be added to improve the properties or facilitate processing of ceramics such as **fluxing agents**, and **refractory ingredients**.

Clay

- Impure hydrated aluminum-silicates originating from feldspar mineral by weathering of igneous rocks
- There are many clay minerals, which contains mixtures of kaolinite, montmorillonite (bentonite), and illite.
- Clays are plastics and moldable when sufficiently pulverized and wet
- Clays are rigid when dry, vitreous when fired at suitable temperature

Feldspar

- A common mineral composed of silica alumina.
- There are 3 major types of feldspars: Potash feldspar, soda feldspar, and lime feldspar.
- Feldspar is an important fluxing constituent in ceramics

Sand

- Also called flint, a natural material composed of granular minerals
- It is composed mainly of silica (in the form of quartz) and calcium carbonate (argonite).

Clays Beneficiation

- Clays vary so much in their physical properties, and in the impurities present (feldspar, quartz, oxides of iron, etc.)
- Thus, it is frequently necessary to upgrade the clay by ***beneficiation process***, which includes:
  - Sand and mica removal
  - Size separation by screening or selective settling
  - Filtration
  - Drying
  - Froth flotation

Additives

Besides the three principal raw materials, different minerals, salts and oxides are used in ceramic production.

- **Fluxing agents**
  - Lower the vitrification, melting or reaction temperatures
- **Refractory agents**
  - Increase the heat resistance of the product

Some Common Fluxing Agents

- Borax ($Na_2B_4O_7 \cdot 10H_2O$)
- Boric acid (H_3BO_3)
- Soda ash (Na_2CO_3)
- Sodium nitrate ($NaNO_3$)
- Pearl ash (K_2CO_3)
- Nepheline syenite [$(Na,K)_2Al_2Si_2O_8$]
- Calcined bones
- Apatite [$Ca_5(F,Cl,OH)(PO_4)_3$]
- Fluorspar (CaF_2)
- Cryolite (Na_3AlF_6)
- Iron oxides
- Antimony oxides
- Lead oxides
- Lithium minerals
- Barium minerals

Some Common Refractory Agents

- Alumina (Al_2O_3)
- Olivine [$(FeO,MgO)_2SiO_2$]
- Chromite ($FeO \cdot Cr_2O_3$)
- Magnesite ($MgCO_3$)
- Lime (CaO) and limestone ($CaCO_3$)
- Zirconia (ZrO_2)
- Titania (TiO_2)
- Hydrous magnesium silicates, e.g., talc ($3MgO \cdot 4SiO_2 \cdot H_2O$)
- Aluminum silicates ($Al_2O_3 \cdot SiO_2$) (kyanite, sillimanite, andalusite)
- Dumortierite ($8Al_2O_3 \cdot B_2O_3 \cdot 6SiO_2 \cdot H_2O$)
- Carborundum (SiC)
- Mullite ($3Al_2O_3 \cdot 2SiO_2$)
- Dolomite [$CaMg(CO_3)_2$]
- Thoria (ThO_2)

Chemical Conversion in Ceramics

- Ceramic processing consist of these general steps:

  Mixing $\rightarrow$ Shaping $\rightarrow$ Firing (700 – 2000°C)

- Such temperatures cause a number of reactions which are the bases of chemical conversion:

  1. **Dehydration:** Chemical water smoking at 150 – 650°C
  2. **Calcination;** e.g., of $CaCO_3$ at 600 – 900°C
  3. **Oxidation** of ferrous and organic matter at 350 – 900°C
  4. **Silicate formation** at 900°C and higher (phase change according to phase diagram)

Chemical Reactions on Clay (Kaolinite) Heating

- Driving off water of hydration
  - occurs at 600 – 650 °C and absorbs much heat
  - leaves an amorphous mixture of alumina and silica

$$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O \rightarrow Al_2O_3 + 2SiO_2 + 2H_2O$$

- Amorphous alumina changes sharply at 940 °C to crystalline form, **γ-alumina**, with the evolution of considerable heat.
- At about 1000 °C, alumina and silica combine to form **mullite** ($3Al_2O_3 \cdot 2SiO_2$)
- At higher temperature, remaining silica is converted to crystalline **cristobalite**.
- Overall reaction:

$$3(Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O) \rightarrow 3Al_2O_3 \cdot 2SiO_2 + 4SiO_2 + 6H_2O$$

Kaolinite — Mullite — Cristobalite

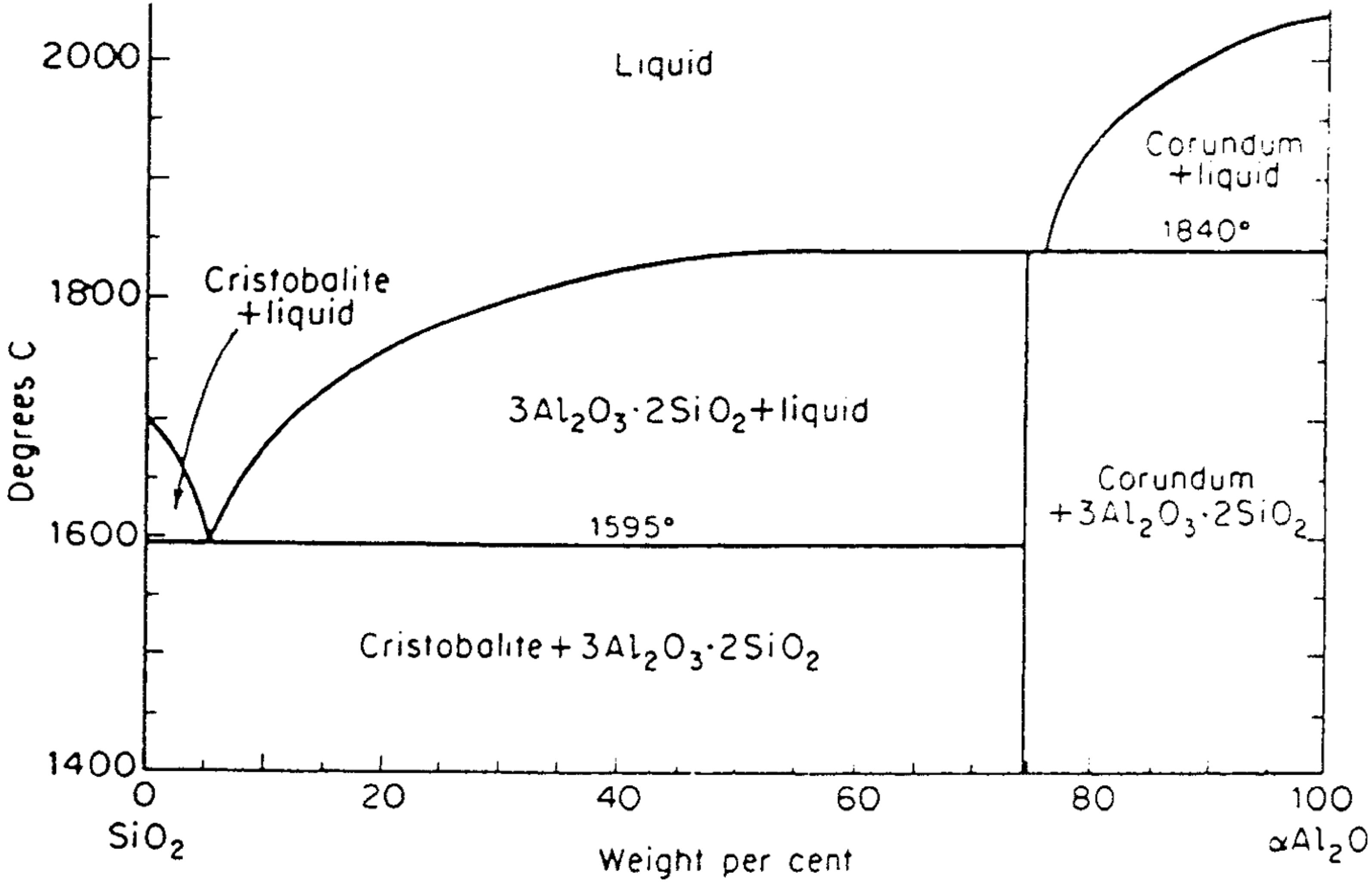


Fig. 6.2. Phase diagram of the system $\alpha Al_2O_3 \cdot SiO_2$. Mullite is $3Al_2O_3 \cdot 2SiO_2$, cristobalite is SiO_2, and corundum is Al_2O_3.

Other Ingredients

- Actual ceramic body contains more ingredients than clay, thus there will be other chemical species beside mullite and cristobalite in the final product.
- Various silicates and aluminates of Ca, Mg, and alkali metals may present.
- The alkali portion of feldspar and most of the fluxing agents become part of the glassy (vitreous) phase of the ceramic body.

Vitrification

- All ceramics undergo certain amount of vitrification (glass formation) during heating.
- Vitrification means progressive reduction in porosity
- Degree of vitrification depends upon:
  - Relative amounts of refractory and fluxing oxides
  - Temperature
  - Time of heating
- Vitreous phase imparts desirable properties to ceramic body:
  - Act as a bond
  - Impart translucency in chinaware
  - etc.

Vitrification

- The degree of vitrification provides the basis of a useful classification of ceramic products as follows:
  1. **Whitewares:** varying amounts of fluxes, heat at moderately high temperatures, varying vitrification.
  2. **Heavy-clay products:** abundant fluxes, heat at low temperatures, little vitrification.
  3. **Refractories:** few fluxes, heat at high temperatures, little vitrification.
  4. **Enamels:** very abundant fluxes, heat at moderate temperatures, complete vitrification.
  5. **Glass:** moderate fluxes, heat at high temperatures, complete vitrification.