FACULTY OF CHEMISTRY
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Ceramic Materials -
forming methods and properties of final elements

LABORATORY PRACTICE

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Introduction

The word ***ceramic*** is derived from the Greek words *kéramos* - ground, clay; *kerameoús* - made of clay. The term covers inorganic non-metallic materials that have been permanently hardened by firing at a high temperature.

Ceramic raw materials (ceramic powders) can be divided into two groups, as shown in Figure 1.

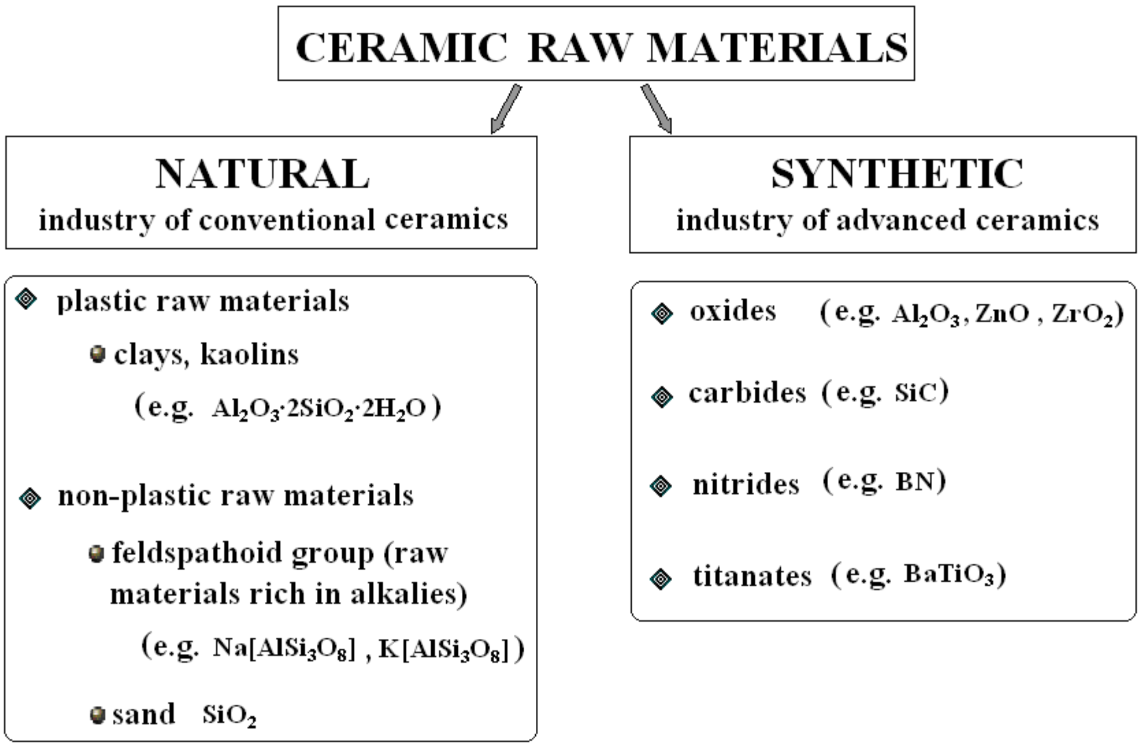


Fig.1. Groups of ceramic raw materials

During fabrication of ceramic products significant structural changes are observed (Fig.2.).

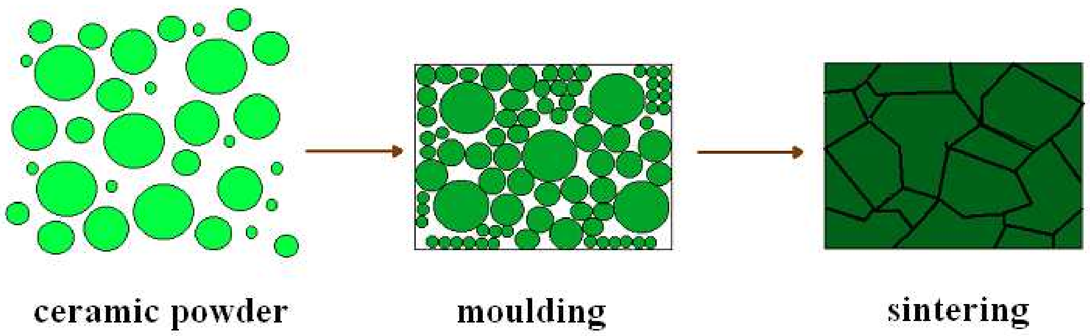
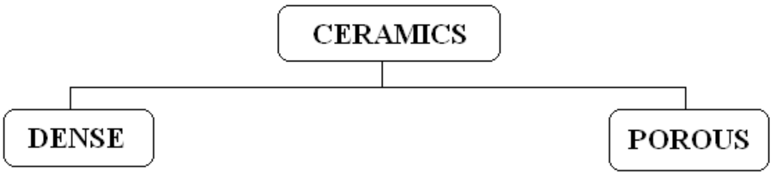


Fig.2. Structural changes in ceramic processing

The first step in ceramic processing is preparing the ceramic powder, the second step is **moulding** (forming). There are many methods of forming ceramics, mainly depending on the final desired shape of a product. The most widespread methods of forming dense ceramics can be divided into several groups. Well-known are also methods of designing porous ceramic materials.



DENSE

1. forming by pressing
- uniaxial pressing
- cold isostatic pressing (CIP)

2. plastic forming
- extrusion, drawing
- injection moulding
- hot moulding

3. forming by casting
- slip casting
- tape casting
- gel casting
- direct coagulation casting (DCC)

4. forming with sintering
- hot pressing (HP)
- hot isostatic pressing (HIP)

POROUS

1. mixing ceramic powder with organic binder and pore-forming substance e.g. sawdust, cellulose and their subsequent burnout

2. polymeric sponge method

3. sintering of properly packed spherical particles of ceramic powder, so that

$$d_{av} = 0,315\ D$$

where d_{av} – average size of a pore

D – diameter of a ceramic particle

The third step in ceramic processing is **sintering**, which is a process of material consolidation caused by heating (Fig. 2). The temperature of sintering is between 2/3 - 4/5 of melting point of the predominant component in the ceramic material. The visible sign of sintering is the shrinkage of the material.

The aim of the laboratory practice is to get acquainted with forming methods in ceramics on the basis of zinc oxide and stoneware clay, and determination the basic properties of ceramic materials. The four methods of fabrication ceramic materials described below allow receiving different types of ceramic products, which are distinguished by different properties and application.

Slip casting is a method for powder-based shaping of ceramic components that has been used for a long time in the traditional ceramic industry for the manufacture of tableware and sanitaryware. Slip casting is occasionally also used in the manufacture of advanced (technical) ceramics. Slips (slurries) are a suspension of ceramic particles in a liquid that is usually water. Slips also contain other materials such as deflocculants (dispersants), pH modifiers, and binders (if the dried slip is to be used for pressing). Slip casting is the process where the slip is poured into a plaster (gypsum) mould and the water is drawn into the plaster, creating a wall of consolidated material (Fig.3.). This can continue until the part is solid, or can be interrupted to make a thin walled part.

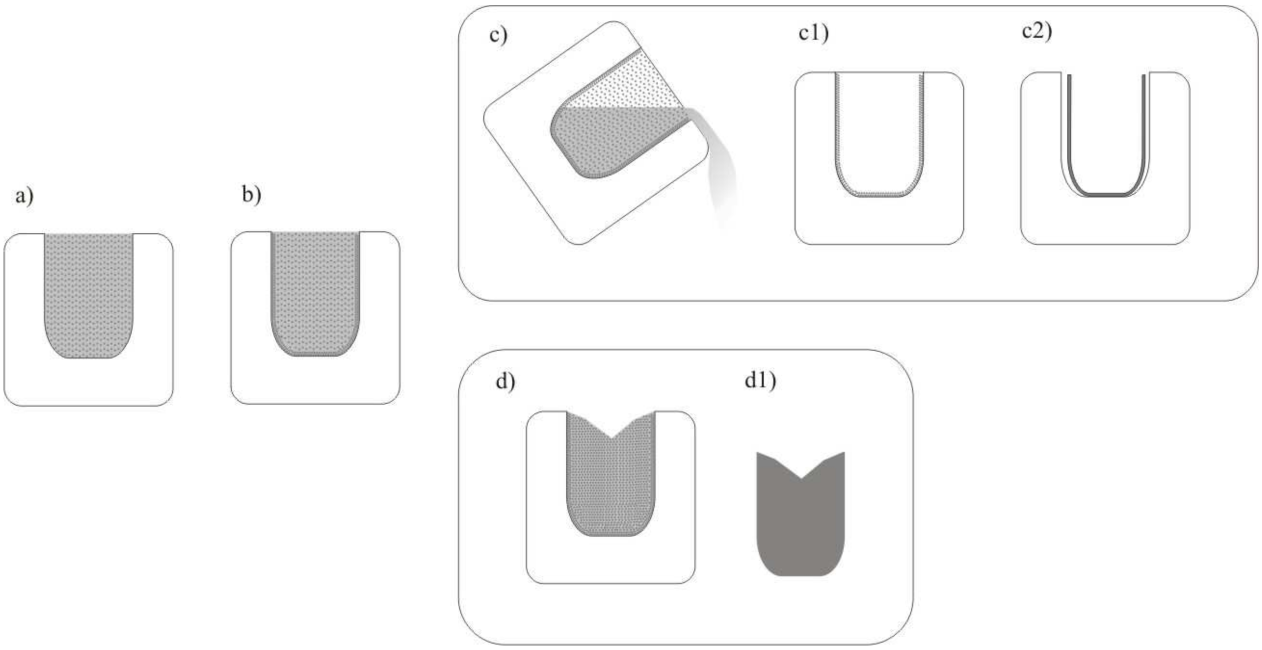


Fig.3. Scheme of slip casting moulding steps: a) plaster mould filled with slurry, b) consolidation of green body by the walls of plaster mould, c) pouring out excess of slurry in order to obtain thin-walled product, c1-2) (thin-walled) product drying (note that there is significant shrinkage of the product in the drying process), d,d1) solid casting.

Tape casting is a forming method of flat, thin tapes, which surface is up to $1m^2$ and thickness of a layer is between 0,1-2,0 mm. This process involves the casting of a slurry onto a flat moving carrier surface. The slurry passes beneath the knife's edge (commonly called doctor's blade), which controls the thickness of a tape. The solvents evaporate to leave a relatively dense flexible tape that may be stored on rolls or stripped from the carrier in a continuous process (Fig.4.).

Many products such as multilayered inductors, multilayered varistors, piezoelectrics, ceramic fuel cells and lithium ion battery components are dependent upon tape casting technology.

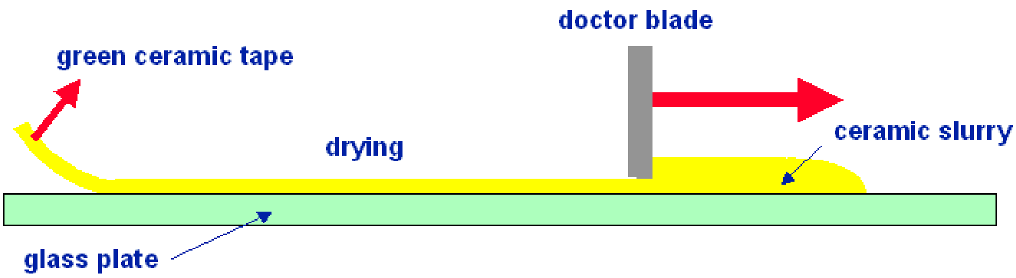


Fig.4. Scheme of tape casting process

Die pressing is widely used in industry as the preferred, inexpensive production process for large numbers of simply shaped ceramic components, such as refractory materials, tiles, electronic ceramics, etc. (note that in this process there is limited geometrical possibilities for the obtained product shape).

In this method a granular powder is put into a steel die where the material is then compacted at pressures by top and bottom punches (Fig.5.). The maximum applied pressure is 350 MPa (in industry, however, for laboratory uses the pressure used can reach even 2 GPa!). Before pressing, the ceramic powder is mixed with appropriate amount of polymeric binder; the commonly used is poly(vinyl alcohol).

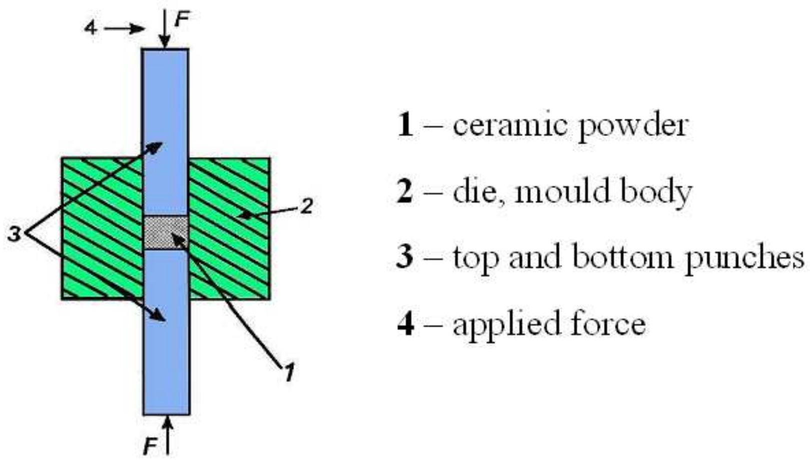


Fig.5. Scheme of die pressing method.

Polymeric sponge method

Porous ceramics are high porosity fragile materials that present cellular structure with closed, open and/or interconnected cells. The increasing interest in porous ceramics is associated mainly with some specific properties, like high specific surface area, high permeability, low density and low thermal conductivity.

The most popular industrial process in fabrication of porous ceramics is replication process, also called polymeric sponge method. It consists in the impregnation of polymeric or natural sponges with ceramic slurry, following by thermal treatment that allows burning out the organic additives, and sintering the ceramic material. As a result the replication of the original sponge is obtained .

The process steps are:

- choice of polymeric sponge
- preparation of ceramic slurry
- immersion of the sponge in ceramic slurry
- removing the excess of the slurry from the sponge
- drying and thermal treatment (burnout of the sponge and consolidation via sintering).

Preparing the ceramic slurry

The slurry consists of ceramic powder with the appropriate addition of solvent, dispersant, polymeric binder and other additives, e.g. plasticizer or surface-active agents.

Dispersant is a substance added to a slurry to promote dispersion or to maintain dispersed particles in suspension. Dispersant prevents also sedimentation of a powder. There are many dispersants used in ceramic technology, for example: diammonium citrate (DAC), ammonium polyacrylate (Dispex A40), KD1 (commercial term)

Polymeric binder is a substance used to bind separate particles together, the most commonly used in ceramic processing are poly(vinyl alcohol) (PVA) or poly(vinyl butyral) (PVB).

Plasticizer is added mainly to slurries in tape casting process in order to make the tape flexible, the examples of plasticizers are: dibutyl phtalate, glycerin.

The important matter in preparing the ceramic slurry is the sequence of adding additives, which is as follows:

1. solvent
2. dispersant
3. polymeric binder
4. other additives (e.g. plasticizer)
5. ceramic powder.

If the slurry is to be mixed in a ball-mill, put all the ingredients (in above mentioned order) into an empty vessel and afterwards, put the balls.

Characteristics of zinc oxide ZnO

In this laboratory practice, the applied ceramic powder is zinc oxide (**ZnO**), due to its attractive properties.

Zinc oxide occurs as white hexagonal crystals or a white powder commonly known as zinc white. In nature it occurs as the mineral zincite. Zinc oxide is for the most part insoluble in water, but is soluble in acids and alkalis.

density – 5,61 g/cm^3

melting point – 1975ºC

Zinc oxide, one of the most important group II–VI semiconductor materials, has attracted much attention and has been extensively investigated during the last few decades. ZnO is a typical semiconductor (with a direct band gap of 3.37 eV), which is an important electronic and photonic material for a wide range of technological applications in many devices. Crystalline zinc oxide exhibits the piezoelectric effect, it is also luminescent and light sensitive.

Zinc oxide finds wide applications in:

- Varistors, which are used to prevent voltage surges in devices like mobile phones
- Sunscreens and sunblocks for the prevention of sunburn due to its ability to absorb ultraviolet light
- Semiconductors
- Gas sensors
- Luminescent devices
- Light-emitting diodes
- Surface acoustic wave filters
- Optical modulator wave-guides
- Catalysts of organic reactions

- Pigments in paints, Chinese white is a special grade of white pigment based on zinc oxide.
- A flux in ceramic glazes, where it can also help prevent crazing.
- A filler for rubber products.
- Coatings for papers.

Stoneware clay

Stoneware clay is a type of clay, composed of hydrous aluminum silicates with a layered structure and very small particle size. Stoneware clays can be fired to a dense body at comparatively low temperatures (ca. 1200ºC). They are heavier, darker and more opaque than porcelain. They are comparatively plastic without showing too much air- and fire-shrinkage. Stoneware remains one of the most common forms of ceramics and is often employed in commercial and industrial products.

Experimental procedure

I. Slip casting.

Preparing the ceramic slurry and examining its rheological properties

1. Preparing the ceramic slurry

- ceramic powder: stoneware clay (200 g)
  concentration of solid phase – 57 wt % of ceramic slurry
- solvent: distilled water - 43 wt % of ceramic slurry
- dispersant: Na_2CO_3 (sodium carbonate) – 0,5 wt % (based on the weight of stoneware clay)

2. Examining the viscosity of the received slurry

a) outflow from Ford cup tester – (average value from 3 measurements)

b) calculation the coefficient of reaching the thickness of the casting **K**

$$\mathbf{K = Fa^2/t}$$

where:

F – temperature coefficient (ratio of outflow from Ford cup in temperature of measurement to outflow in temperature 20°C)

a – thickness of the casting

t – time to reach the desirable thickness of the casting: e.g. 2 and 5 minutes.

II. Tape casting.

Receiving the ceramic tapes in non-aqueous system

1. Preparing the ceramic slurry

slurry A:

- ceramic powder: ZnO (10 g); concentration of solid phase – 53 wt % of ceramic slurry
- binder: poly(vinyl butyral) PVB 4000-2 – 5 wt% (based on the weight of zinc oxide)
- plasticizer: dibutyl phthalate - 8 wt% (based on the weight of zinc oxide)
- dispersnat: KDI – 1 wt% (based on the weight of zinc oxide)
- solvent: azeotropic mixture of trichloroethylene with ethanol

slurry B:

- ceramic powder: ZnO (10 g); concentration of solid phase – 53 wt % of ceramic slurry
- binder: polyvinyl butyral PVB 4000-2 – 5 wt% (based on the weight of zinc oxide)
- dispersnat: KD1 – 1 wt% (based on the weight of zinc oxide)
- solvent: azeotropic mixture of trichloroethylene with ethanol

2. *Mixing the slurry in the teflon mixer for 90 minutes*
3. *Pouring the slurry on the hydrophobic polyester base*
4. *Drying the tapes for 24 h in the room temperature*
5. *Measuring the density of the dry tapes*

III. Polymeric sponge method

1. Preparing the ceramic slurry
   - ceramic powder: ZnO (60 g), concentration of solid phase – 70wt % of ceramic slurry
   - solvent: distilled water
   - dispersant: DAC (diammonium citrate) - 0,5 wt % (based on the weight of zinc oxide)
   - binder: poly(vinyl alcohol) PVA – 1 wt % (based on the weight of zinc oxide), added as 10% solution
   - octanol (as foam reducing agent) – 1 drop
2. Immersion sponges in ceramic slurry and removing the excess of the slurry
3. Drying and sintering the material
4. Determination the volume of ceramics and open porosity on sintered elements

Formulas for calculations for polymeric sponge method

Volume of ceramic V_c

$V_c = m/d$

where: m – mass of sintered element

d – density of ZnO (5,61 g/cm^3)

Open porosity P_o

$P_o = (V - V_c)/V\ 100\%$

where: V – volume of an element

IV. Die pressing

1. Preparing the granular powder:

a) mixing ZnO powder with polymeric binder, poly(vinyl alcohol) (PVA) – 10 wt % of 5 % PVA solution

b) mixing ZnO doped with one of mentioned oxides (Bi_2O_3, Fe_2O_3, MnO_2, Cr_2O_3, CoO) with 10 wt % of 5 % PVA solution

2. Pressing from each powder 5 rectangular blocks of dimensions: 30x10x5 mm

3. Determination of mass and dimensions of prepared blocks and calculation of relative density

4. Sintering of blocks in one of mentioned temperatures: 1050ºC, 1100ºC, 1150ºC

5. Determination on sintered clocks:

a) linear and volumetric shrinkage

b) apparent density, open porosity and water absorbability

c) bending strength

Formulas for calculations for die pressing method

Linear shrinkage S_1 and volumetric shrinkage S_2

$S_1 = (l_0 - l_1)/l_0 \cdot 100\%$

$S_2 = (V_0 - V_1)/V_0 \cdot 100\%$

where: l_0 – length of block before sintering

l_1 – length of block after sintering

V_0 - volume of block before sintering

V_1 – volume of block after sintering

Relative density d_r and apparent density d_a

$d_a = m_s/(m_w - m_{ww})$ [g/cm^3]

$d_r = d_a/d$ [%]

where: m_s – mass of block after sintering

m_w – mass of block waterlogged weighed on air

m_{ww} – mass of block waterlogged weighed in water

Water absorbability N:

$N = (m_w - m_s)/m_s \cdot 100\%$

Open porosity P_o:

$Po = (m_w - m_s)/(m_w - m_{ww})100\%$

Bending strength σ_B:

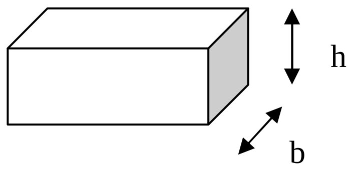
$\sigma_B = 3Pl/2bh^2$ [MPa]

where: P – force causing destruction of a block [N]

l - distance between supports of form (1,5 cm)

b – width of a block

h – height of a block



Densities of other oxides:

Bi_2O_3 – 8,90 g/cm^3

Fe_2O_3 – 5,11 g/cm^3

MnO_2 – 5,03 g/cm^3

Cr_2O_3 – 5,22 g/cm^3

CoO – 5,68 g/cm^3

The bases to pass the laboratory practice (except the test) are: presence, active participation in practice and writing a short report, which will be then marked. The report should include: results of measurements, required calculations and conclusions.

Literature

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