

„The Basics of Materials Science – Ceramics” – laboratory 1
for first year students of the Faculty of Mechanical Engineering and Robotics

Classical technology of ceramics is based on powders processing

The prevailing part of ceramic products have **polycrystalline** structure. Those products are prepared according to specific technological scheme. That scheme bases on processing of starting powders, namely on shaping them into desired form and subsequent further consolidation occurring at relatively high temperature, which is called firing or sintering. In some cases operations of final cutting, polishing or machining are required. In such scheme, applied in practice in different variants, bricks, tiles, sanitary wares but also cutting tools or turbocharger rotors of modern combustion engines are produced. The practical example of mentioned scheme is illustrated in figure below.

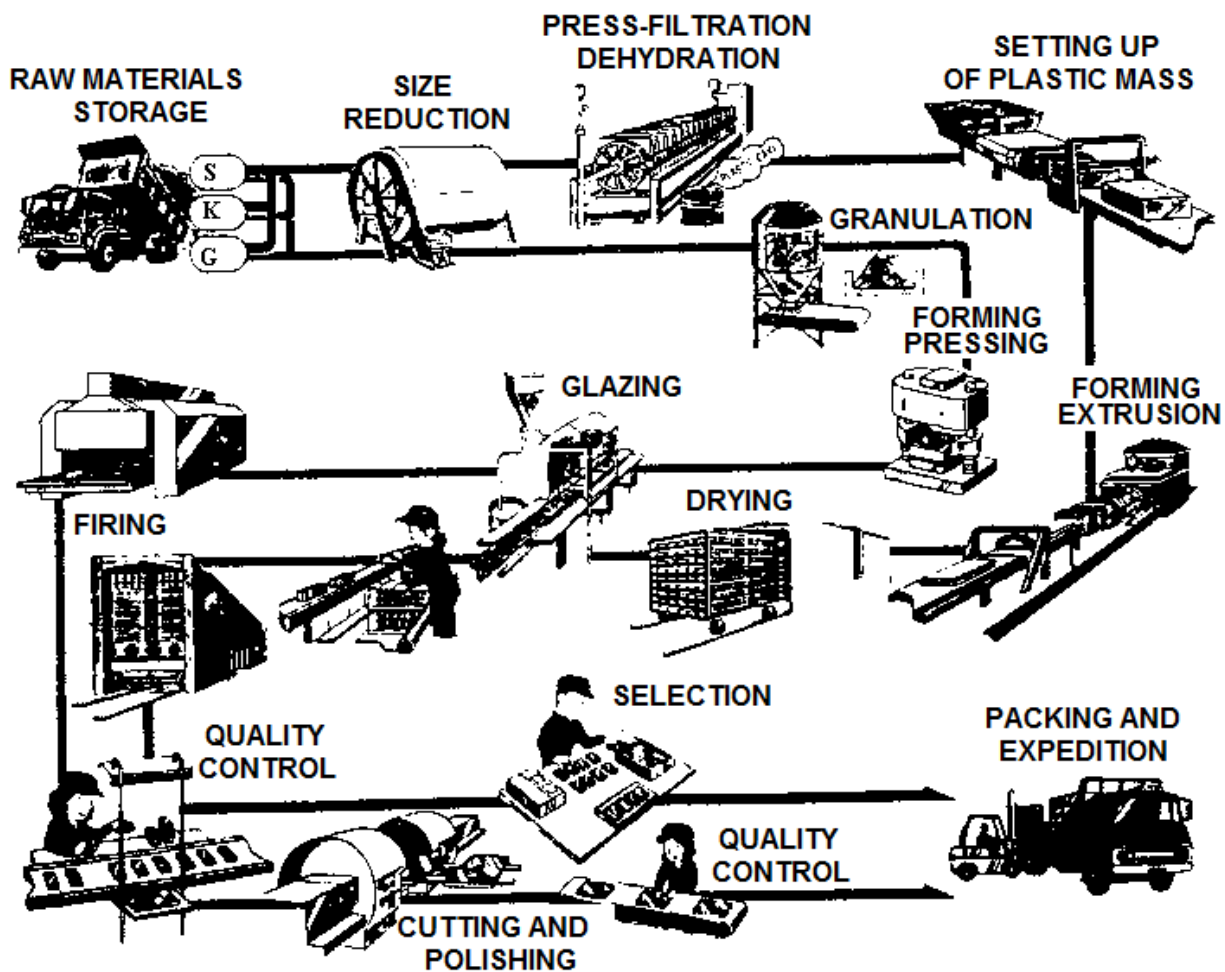


Fig. 1. Variant of technological scheme of ceramic tiles production.

At the end of such technological cycle is a product with required shape, dimensions, structural properties (density, porosity), mechanical properties (hardness, stiffness, fracture toughness) and other useful properties depending of phase composition (chemical durability, electrical-, optical- and magnetic- parameters, wear resistance).



Fig. 2. Assortment of ceramics products for technical applications produced by CEREL (on the top) and DORST (at the bottom).

Each of mentioned technological stages influence the final properties of the products. Level of the size reduction (the mean grain size and the grain size distribution) of the starting powder, its phase and chemical purity, shape and surface state of the grains decide how the powders behave during forming process. For example, powders with highly diversified grain size distribution could segregate during forming giving non-uniformly densified products.

Basic definitions of powder description:

crystallite – a single, crystallographically uniform element of the powder; **aggregate** – a set of crystallites with common boundaries; **agglomerate** – a set of crystallites or aggregates contacting pointwise; **grain size** – the size of single elements of the powder. The **grain size distribution** is also important for powder characteristic.

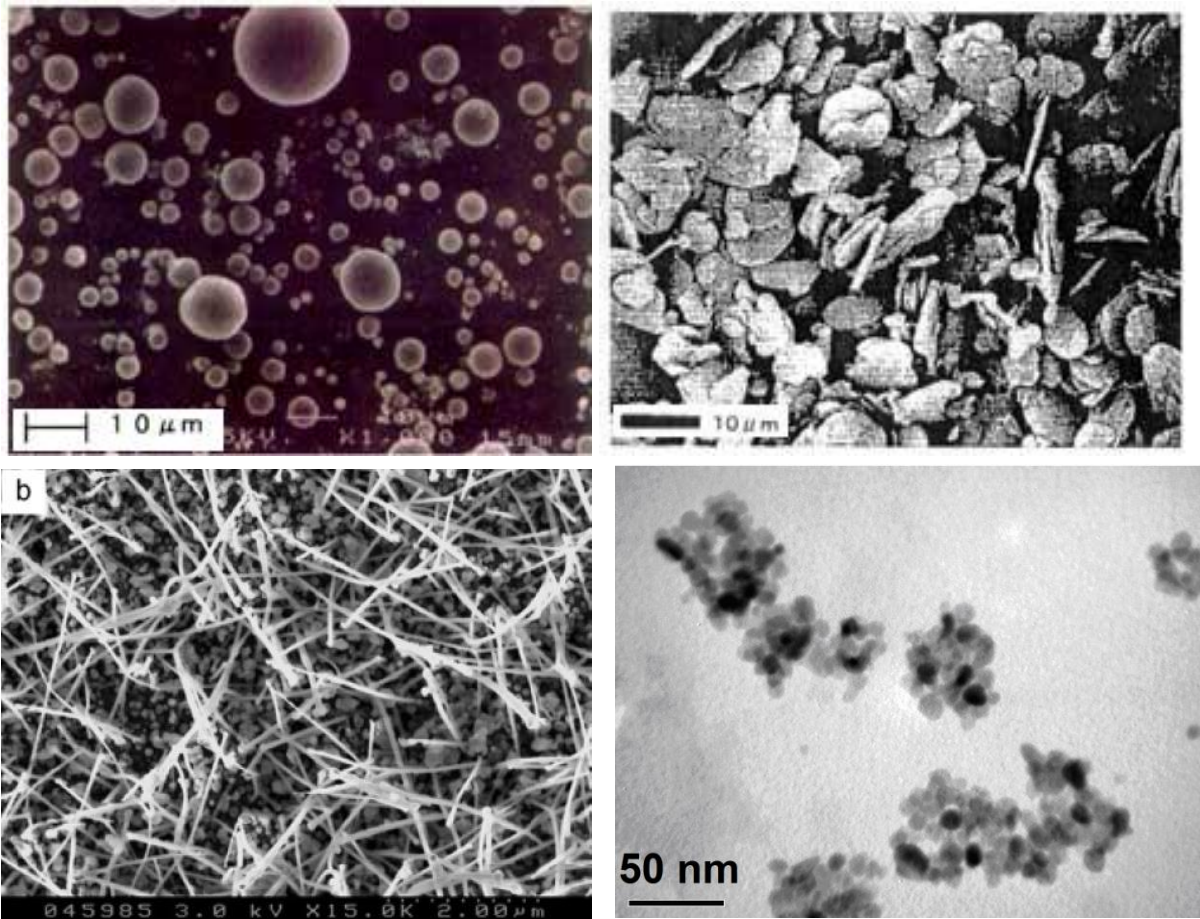
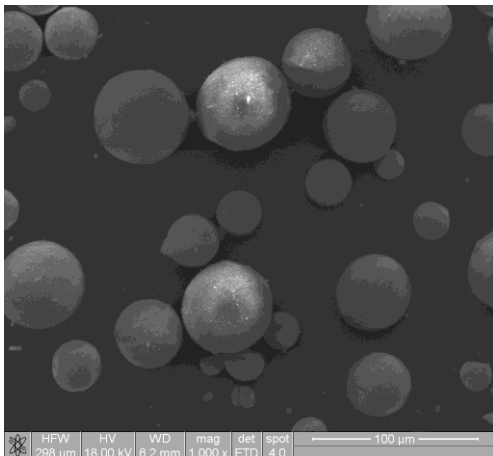


Fig. 3. Example microscopic images of technological ceramic powders.

Among many **methods of ceramic powders shaping (green-body preparation)** one can distinguish three main groups: **pressing**, **slip casting** and **plastic forming**. Each method can be applied in many technological variants, depending the type and shape of final product and also its phase composition and properties.

Pressing techniques are utilized for preparation of relatively simple shapes. The pressing is easy to automation and this fact makes it favourable from the economic point of view. In case of pressing, one uses the **granulated form of powder** – specially agglomerated to form granules of regular shape and similar size. Typical granulate contains some technological additives which assure better forming performance (lubricants) and also mechanical parameters of formed products (binders).



Sometimes, during granulation process one can add compounds necessary during firing (sintering aids). The most popular and effective way of granulation is drying of ceramic particles suspension with a spray-dryer. Such a method gives the possibility of precise control of granule powder properties and very uniform incorporation of technological additives.

Fig. 4. Granulated alumina powder.

In a wide use are techniques of **pressing in stiff forms**, made of steel or so called sintered carbides (tungsten carbide cemented with cobalt), by uniaxially applied load. High accuracy of details mapping and perfect condition of surfaces and edges of shaped products are the main advantages of that type of pressing.



Fig. 5. Ceramic cutting inserts

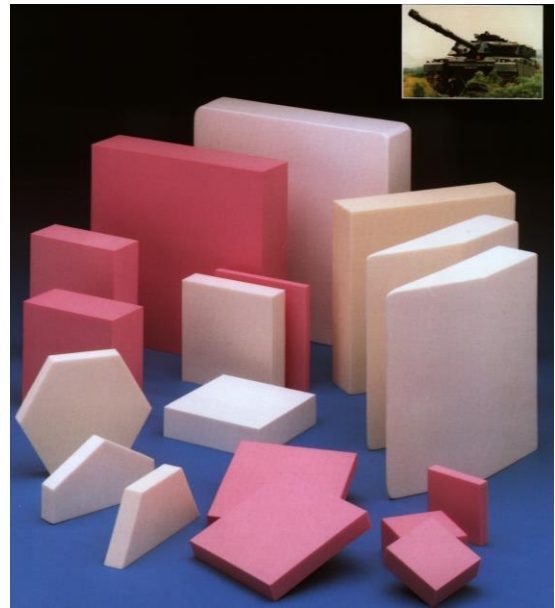


Fig. 6. The armour plates for tanks protection.

Isostatic pressing is realized by multi-directional load application to the elastic forms (polymers, elastomers) containing granulated powder. Such a treatment ensures high densities of formed green-body to be achieved. That shaping method expands an assortment of shapes possible to form, especially isostatic pressing is useful for long products.

Plastic forming demands of special mass preparation. Such mass can be deform under relatively low load. The simplest variant of such mass is composed of the solid powder and water in sufficient amount (15-20%), also some **plasticizers** may be added. Such prepared mass can be shaped by **extrusion** or **pressing**. The relatively high content of water in formed product implicates **drying** (105-115°C) as a separate technological operation before firing.



Fig. 7. Oil lamps from the first centuries A.D. formed with humid, plastic clay.

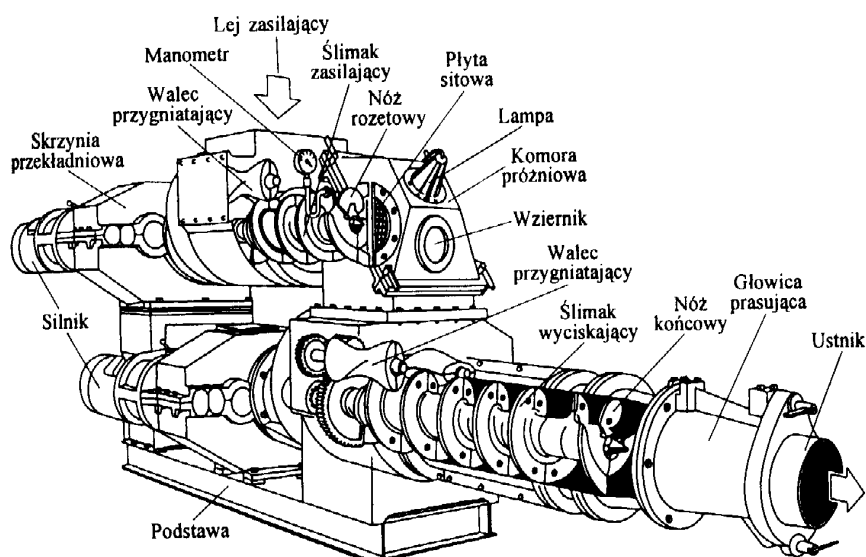


Fig. 8. Scheme of extruder for plastic masses shaping.

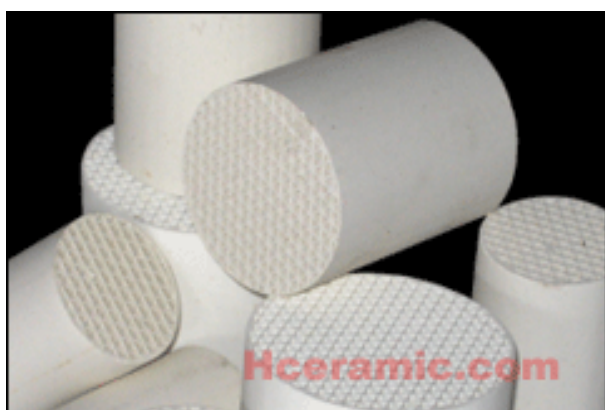


Fig. 9. Automotive catalyst carriers made of cordierite ($Mg_2Al_3(AlSi_5O_{18})$) by extrusion (MeiJing Ceramic).



Fig. 10. Insulating protector (electro-porcelain) formed by turning of extruded cylinder (Zapel).

The more complicated variants of plastic formation are based on **injection techniques** at ambient or elevated temperatures (thermoplastic forming). Such technologies demand quite a different type of plasticizers (waxes, resins), which have to be removed before firing. Usually, simple drying is not enough because those substances do not evaporate at water boiling temperature. It is necessary to apply thermal decomposition process (at few hundreds °C). Such decomposition should be conducted with care due to possible cracks or other flaws in the green body, due to sudden release of the gases.

The following advantages of plastic formation can be pointed: possibility of manufacturing extremely complicated shapes, perfect mapping of small details (very important for parts of machinery manufacturing). Disadvantages lie in high costs of instrumentation (injection forms).

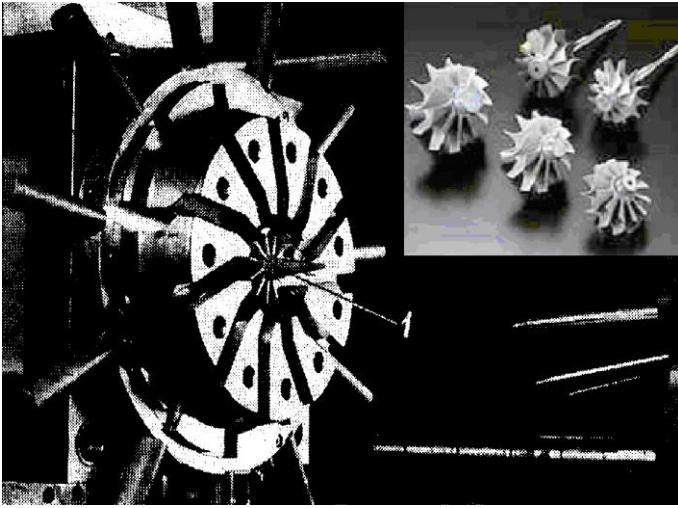


Fig. 11. Injection form and turbocharger rotors green bodies made of silicon nitride Si_3N_4 .



Fig. 12. Dental implant made of tetragonal zirconia polycrystals (ZrO_2) using injection technique (Nobel Biocare).



Fig. 13. Different products of technical ceramic shaped by injection technique (Kyocera).

Slip casting is a technique relatively cheap. It allows to manufacture products with significant complication of shapes (table porcelain) and with relatively large size (sanitary ware). The slip casting requires filling a gypsum or polymeric mould with suspension, containing ceramic powder, water and additives (deflocculants, surfactants, stabilizers, binders, etc.).



Fig. 14. Products shaped by slip casting using gypsum mould – XVIII century porcelain jug from Meissen (left), technical ceramic made of silicon carbide SiC (JinHong Group)(right).



Fig. 15. Stand for high-pressure casting of sanitary ware in acrylic forms (Sacmi Forni).

Depending the way of suspension destabilization (casting) one can distinguish different types of slip casting. The most important are:

- pressureless slip casting in gypsum forms – the most traditional way of slip casting. It allows to achieve products with very complicated shapes,
- high pressure slip casting in acrylic forms – the best method for large products (sanitary ware),
- press filtration,
- gel-casting – monolithic products could be formed with this method.

The slip casting forming also requires drying before firing (sintering).

As mentioned above, each technique of ceramic powder formation gives a green body which is in fact, a set of ceramic phase grains formed in desired shape but these grains are weakly connected by frictional forces supported the binder presence. In this stage of manufacturing the products have relatively low mechanical strength and large porosity (up to 20 – 60%).

Final properties and dimensions are reached during **sintering (firing)**. This term describes heat treatment of the green body at temperatures lower than melting point given substance. During sintering **the set of grains connecting only pointwise transforms to polycrystalline structure with grain boundaries**. Final **microstructure** of the ceramic product is formed.

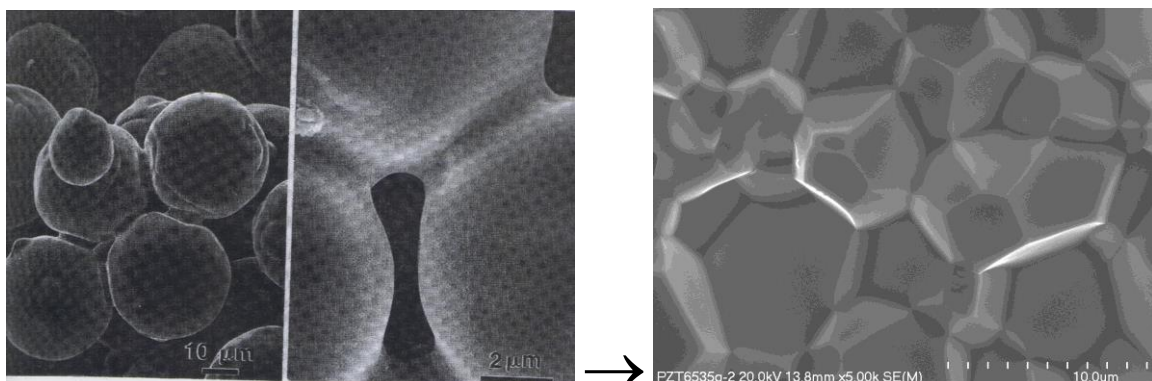


Fig. 16. Scheme of transformation from pointwise contacts to grain boundaries in dense polycrystal.

Usually, the sintering is assisted by **shrinkage connected with porosity elimination**. Characterisation of the final microstructure includes description of grains size, grain size distribution, grains shape, pore size and pore size distribution.

Practically, the most often sintering is applied as **pressureless sintering**, meaning the heating of product undergo at atmospheric pressure. Sintering temperature applied influences atomic diffusion intensity and the diffusion itself eliminates the pores in the final product. Other significant factors affecting sintering effectiveness are: sintering atmosphere (in case of nitrides or carbides sintering) and technological regime (heating rate, the time of soaking at maximum temperature, cooling rate).

There are some special sintering techniques dedicated for hardly sintered systems, or used exclusively to enhance sintering rates. **Hot-Pressing (HP)** is a method of sintering with stiff mould (for example graphite one) under uniaxially applied load - pressure. **Isostatic Hot-Pressing (HIP)** is a method of sintering under multidirectional pressure; **forging** means sintering under uniaxial load with a possibility of free sinter deformation; **microwave sintering** occurs when fast heating is induced by microwaves; **spark plasma sintering** takes place when heating is induced by electric current flowing through the powder additionally causing plasma discharge between powder particles.

Depending of sintered phase sintering temperature could be different. The most of oxide phases can be sintered in the range 1200 - 1700°C. Carbides demands much higher temperatures (over 2000°C) to achieve a dense microstructure.

Materials microstructure

What microstructure is? The term is connected with a basic tool of materials structure observation – optical microscope. After that, a material structure visible in microscope was named **microstructure**. The resolution of optical microscope is not higher than $1\ \mu\text{m} = 10^{-6}\ \text{m}$. That scale roughly corresponds to the smallest grains in classical ceramic materials. However modern materials have grains even nanometric in size. Such small objects can be observed only with electron microscope – a scanning one (SEM) can work with magnifications up to 100 000x and the transmission one (TEM) gives even higher magnifications, up to 1000 000x.

In this statement we are limited to relatively simple case of monophasic polycrystalline material which is a set of grains with random crystalline orientation separated by grain boundaries. Such a type of material is achieved by powders sintering. Samples of different ceramic microstructures are collected below in Figures 17 – 22. It is worth to notice that concepts and methods used for material microstructure description have to be adjust to a type of microstructure – polycrystalline, glassy, porcelain like, cement like, etc.

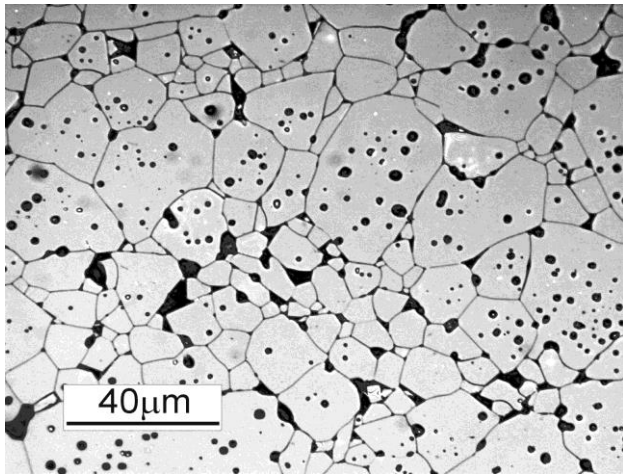


Fig. 17. Micrograph of etched and polished section of magnesia-zinc ferrite ($(\text{Mg,Zn})\text{Fe}_2\text{O}_4$) with visible grains (bright areas), grain boundaries (dark lines) and pores (small, dark areas).

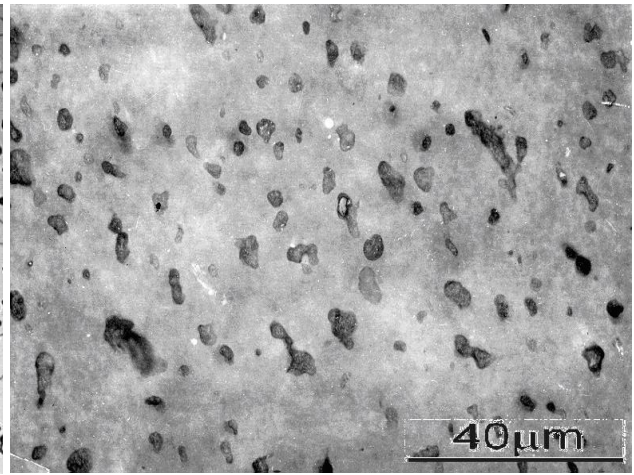


Fig. . 18. Micrograph of non-etched polished section of steatite ($\text{Mg}_3(\text{OH})_2\text{Si}_4\text{O}_{10}$). One can distinguish only pores (dark areas) surrounded by solid phase.

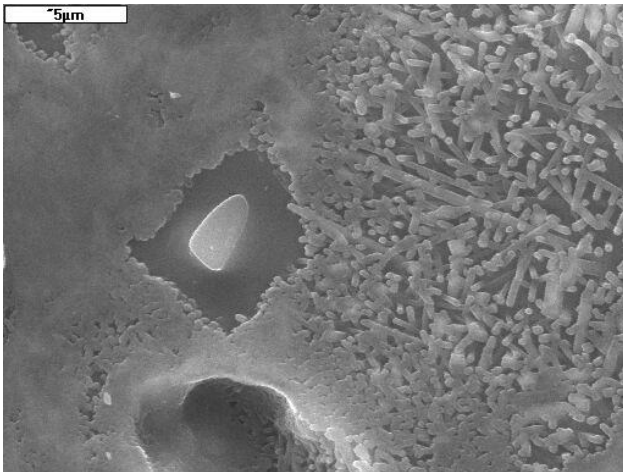


Fig. 19. Micrograph of etched polished section of porcelain. Clearly visible is quartz grain surrounded by glassy phase and mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) matrix. This matrix consists a flaky mullite (grey area on the left side) created by thermal transformation of kaolin ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) and a spine mullite (darker areas) crystallized from glassy phase – melted feldspar (orthoclase $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$).

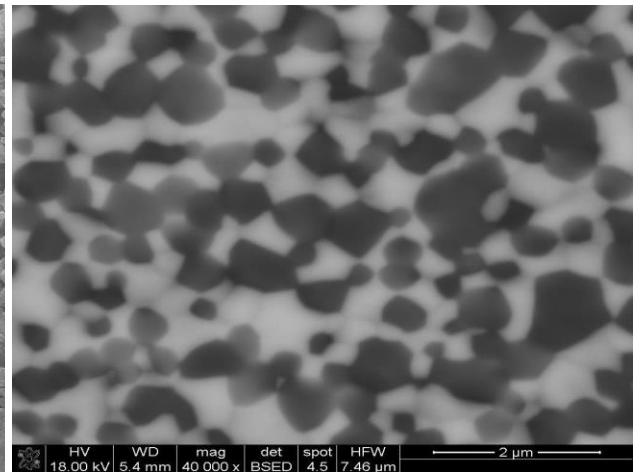


Fig. 20. Micrograph of microstructure of two-phase composite in alumina (Al_2O_3 – dark grains) – zirconia (ZrO_2 – bright grains) system with sub-micro (from tens to hundreds nanometers) grain size.

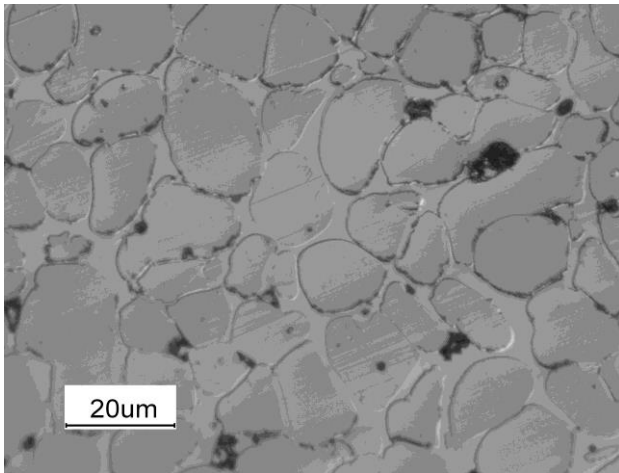


Fig. 21. Micrograph of etched and polished section of niobium carbide (NbC) sintered with liquid phase. That phase after crystallization is composed of chromium carbide (Cr_7C_3) – areas fulfilling inter grains areas.

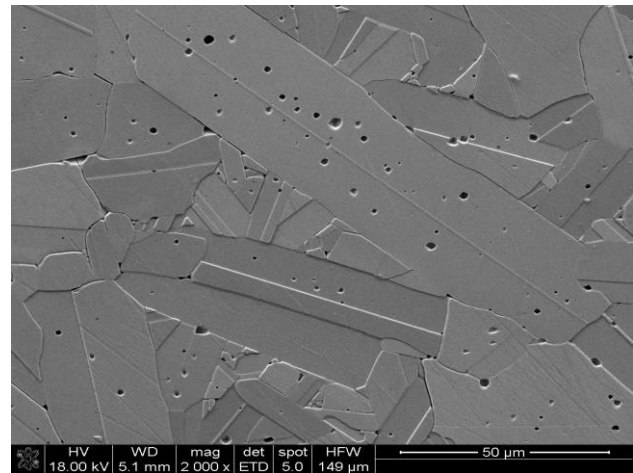


Fig. 22. Micrograph of etched and polished section of sintered monophase tungsten carbide (WC). Small spherical, dark objects correspond to pores.

Microstructure of materials is so interesting because many properties (mechanical, thermal, electrical) are determined by microstructure. Microstructure is tailored by modification of technological process, that means one can change material properties by adjusting manufacturing conditions.

Quantitative description of microstructure

Detailed description of material microstructure requires **quantitative** approach, that means description by **numerical parameters**. Only the quantitative description enables proper determination of correlation between material structure and parameters of its manufacturing. Difficulties in proper description of ceramic and metallic materials are connected with their non-transparency. Investigation of the structure of these materials could be provided only on **polished sections**. Such sample is especially prepared for microscopic observation. Surface of polished section has to be flat and smooth. Preparation of the samples consists of grinding and polishing with special materials (diamond pastes) and instrumentation. Prior to microscopic investigations polished surfaced are often etched (thermally or chemically) to visualize grain boundaries. Without etching one can see only flat cross-sections of three-dimensional grains.

Stereology is a branch of science, describing three-dimensional sets of solids by measurements or counts made for two-dimensional cross-sections of mentioned sets of solids.

Parameters describing microstructure could be achieved by measurements (**metric parameters** – for instance grain size) or by counting (**topological parameters** – for instance a number of particles for area unit). Stereology fixes relations between three-dimensional space parameters $R^{(3)}$ and parameters of spaces $R^{(0)}$, $R^{(1)}$ and $R^{(2)}$.

One can distinguish parameters:

- **local** (statistical), giving the mean characteristic of one particle in defined space (the mean volume of particle \bar{V}),
- **integral** (global), characterizing numerically a set of defined particles in relation to unit of measure in given space (a surface of particles in 1 mm^3 of material S_V or volume fraction V_V).

The one of basic integral parameters is **relative volume V_V** , also called **the volume fraction**. This parameter is used for description of multiphase materials and serve for definition of relative amount particular phase in the material. The term “phase” has the context different of this used in thermodynamic. It means homogeneous part of the material. It is worth to notice that determination of volume fraction of any phase demands identification of this phase on polished section. Such identification could be done by diffraction or spectroscopic method (XRD, EDS).

If material is composed of n phases, the volume fraction of i -th phase $V_V(i)$ is defined as a ratio of the volume occupy by this phase V_i and the whole material volume V :

$$V_V(i) = V_i/V \quad (1)$$

Practically determination of volume fraction basing on statement, that a fraction occupy by i -th phase in material volume V_V , a fraction occupy by this phase on surface of cross-section A_A (**surface fraction**) and a fraction of length of unit interval laying on flat cross-section of this phase grains L_L (**linear fraction**) are equal each other.

$$V_V = A_A = L_L \quad (2)$$

In real material the phase composition could not be equal in a whole sample volume. During measurements of linear or surface fractions some fluctuations occur, that means that they are only statistically constant. It is very important for proper results to have material homogeneous in structure or being isotropic (random distribution of phases). Also the proper choose of representative sample for microstructural investigation is important.

Methods of volume fraction determination

Planimetric method

Determination of volume fraction of selected phase β in the material depends on the measurement of its surface area A_β on the plane of polished surface. This area has to be related to whole surfaces of investigated sample A :

$$V_V(\beta) \cong A_\beta/A \quad (3)$$

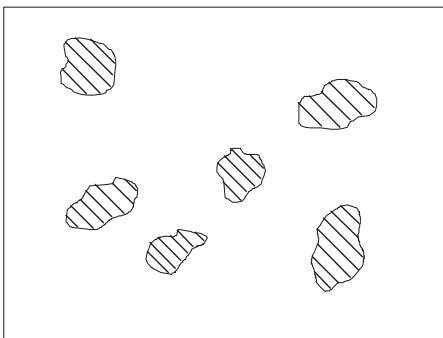


Fig. 23. Illustration of planimetric method of volume fraction measurement. At the model image two phases are visible: particles (areas with lines) distributed in the matrix (white area). Particle volume fraction is measured as a sum of surface areas of every particle divided by the area of whole visible domain.

Linear method

The randomly oriented line (secant) is guided through polished surface area. This secant cuts n_k grains of β phase on length of measurements l . One have to measure the secants length of grains cut with the secant c_{ik} . This procedure is repeated n times for different secants laying on polished surface.

Let's introduce following designation:

$\bar{L}_L(\beta)$ – the volume fraction of β phase calculated on the base of n secants measurements,

c_{ik} – secant of i -th grains of β phase on k -th secant ($k = 1, 2, 3, \dots, n$ is a number of secant; $i = 1, 2, 3, \dots, n_k$ is a number of chord on secant).

The volume fraction of β phase in the material could be expressed by the formula:

$$V_V(\beta) \cong \bar{L}_L(\beta) = (1/nl) \sum_i \sum_k c_{ik} \quad (4)$$

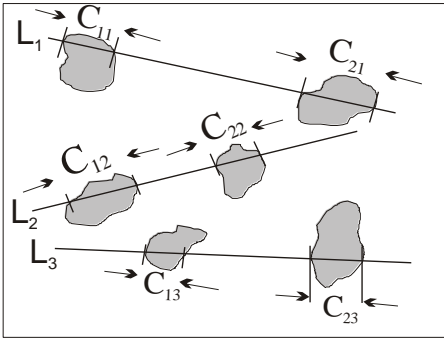


Fig. 24. Illustration of line method of volume fraction measurement. Randomly oriented secants (three in this example: L_1, L_2, L_3) are drawn on sample image and the length of particular chords is measured. It is possible that random secant overlaps no particle.

Point method

The point method with conception referring to planimetric method. Increasing of number of points (decreasing of distance between them) lead to the planimetric method.

The random point method

Measurements depends on random projection of points of the polished sample plane in such a way, that points are statistically distributed on the whole plane. The volume fraction of β phase is equal of the ratio of number of points hitting β phase P_β to the whole point number P :

$$V_V(\beta) \cong P_\beta/P. \quad (5)$$

Net method (see fig. 25)

In this type of point method the regular grid of points is randomly projected on the polished surface. If “ s ” means the number of points in the net and “ k ” means multiplication factor (number of random applications of the grid of points), the volume fraction is calculated as the ratio of the number of points overlapping particular phase to the whole number of projected points:

$$V_V(\beta) \cong \bar{P}_P(\beta) = (1/ks) \sum_i P_i(\beta) \quad (6)$$

where:

$\bar{P}_P(\beta)$ – the volume fraction of β phase calculated with k net projection,

$P_i(\beta)$ – the number of points hit β phase in i -th projection of net composed of s points.

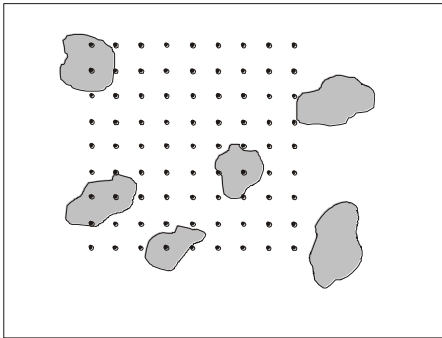


Fig. 25. Illustration of the net method of volume fraction measurement. A grid of points is randomly applied on sample image and points overlapping particular phases are counted.

The basic definitions used for densification description

The basic description of every real polycrystalline material requires determination its densification. The immanent attribute of every substance is **real or physical density (d_{rz})**, that means **density in monolithic state (without pores), expressed in g/cm^3** .

The real density could be determined by different normalized methods (pycnometric, roentgenographic) which demand adequate prepared samples.

In practice materials have some amount of porosity. Their density, that means the mass – volume ratio, is called **apparent density, (d_p [g/cm^3])**. The methods of apparent density determination depend on sample weighing and description its volume (with pores). If sample have simple shape it could be done by careful dimension measurement. If sample shape is not regular other methods have to be applied (hydrostatic weighing).

The ratio **$(d_p/d_{rz}) \cdot 100\%$ is called relative density d_{wzg}** . It defines the level of „space filling” by mass in the sample in relation to monolithic material.

The total porosity is defined as **$P = 100\% - d_{wzg}$** .

Pores in material could form isolated voids (closed ones) or a net of channels connected each other and with external atmosphere (open ones). Often in the material the both types of porosity are present. Their proportion could be determined by comparing relative density and **absorbability** using the liquid showing good wettability of the material (water, alcohols). The wettability determination allows to calculate of open pores amount. The difference between total porosity and open porosity is closed pores. There is no direct methods for determination of this type of pores.

The significant supplement of the knowledge on material porosity **could be the pore size distribution analysis**. It can be measured using mercury porosimetry or capillary condensation method.

Because materials in the form of powder play a key role in ceramic technologies, except the knowledge of grain size distribution also important is the knowledge of initial powder densification. The basic terms of such description are **freely settled powder density (d_{nas} , [g/cm^3])** – the density which reaches the powder freely poured into define volume and **tapped density (d_{nas-us} , [g/cm^3])** – the density of the powder subjected to sedimentation under normalized shaking (vibrations). The knowledge of such parameters is helpful for predicting of powder behaviour during forming and makes possible optimal design of forming tools.

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