

„The Basics of Materials Science – Ceramics” – laboratory 2

Faculty of Mechanical Engineering and Robotics, 1st year

“Mechanical properties of ceramic materials”

Introduction

Under applied external force all bodies deform. When the forces are moderate, materials undergo gradual deformation, elongation or contraction, which is proportional to the load applied. After the load is removed a sample recovers its original shape. Such reversible strain is called **elastic strain**.

For moderate strains all materials behave alike, except that the strain due to a given load is different for various materials. In order to distinguish between the behaviour of individual materials, **material constants** are introduced. In the range of strain to stress proportionality a relation between the normal or shear (tangential) stresses and the strains is given by Hook's law:

$$\sigma = E \cdot \varepsilon \quad (1)$$

$$\tau = G \cdot \gamma \quad (2)$$

where:

E – Young's modulus,

G – shear modulus (the stiffness constant),

ε – elongation strain,

γ – tangential strain,

σ – normal stress,

τ – tangential stress.

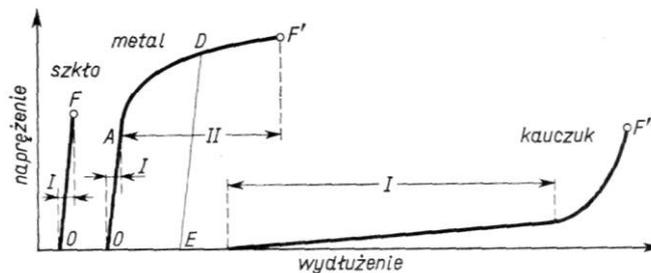


Fig.1. Relationship between strain and stress for various solids: I – elastic strain, II – plastic strain

During an uniaxial elongation under tensile loads of ideally elastic and isotropic solid a lateral contraction also takes place. If the strain along the direction of the load equals ε , the lateral strain is $-\nu\varepsilon$. The minus sign means that the lateral strain (elongation) and the longitudinal strain (contraction) are of opposite sign. The constant ν is known as *Poisson's ratio* and like E and G depends of a kind and structure of material.

Significant differences in the behaviour of bodies occur under larger stresses. Fig 1 shows the relationship of stress vs. strain for various materials. The strain in the majority of ceramics terminates in a sudden decohesion of the material at point F . On the other hand, most of metals don't undergo a sudden decohesion at certain stress but, starting from point A , they undergo a deformation which increases with time. The deformation arising from stresses higher than A is permanent, i.e. it doesn't disappear after removal of the load and it is called **a plastic strain (a plastic deformation)**. The point A is defined as **a yield point**. Bodies which fail at deformations lower than those corresponding to the yield point are called **brittle bodies**, whereas bodies which are capable for plastic deformations are defined as **plastic bodies**.

Deformation in the atomic scale consists in forced movement of an atom from its equilibrium position (state of minimal potential energy). In case of crystal, in which an atom interacts with neighbouring atoms such movement leads to displacement of the whole atomic layers. For small displacements the energy used to move atoms accumulates in the structure (elastic strain energy), and after removal of the load the atoms come back to their equilibrium positions. In such case we talk about **elastic strains (elastic deformations)**.

Such mechanism may be described considering potential energy changes in a bi-atomic model. Potential energy (V) of interaction between two atoms vs. the distance between them (r) (Fig. 2) may be represented as a sum of attraction energy and repulsion energy:

$$V = -\frac{A}{r^n} + \frac{B}{r^m} \quad (3)$$

where:

A and B – proportionality constants of attraction and repulsion respectively
m and n – exponents

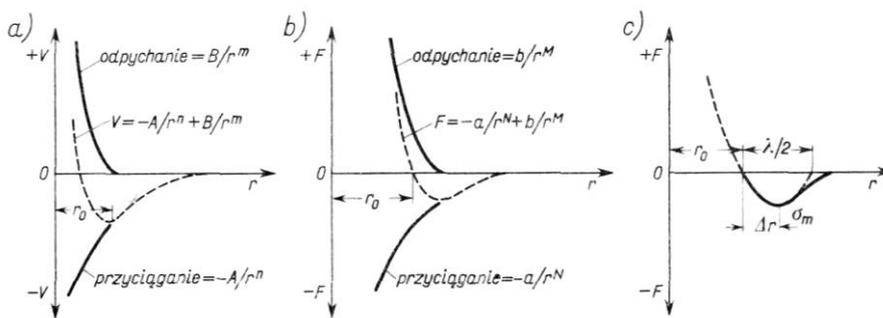


Fig.2. Condon-Morse curves representing potential energy changes vs. interatomic distance r

The distance corresponding to the minimum of potential energy is an equilibrium distance r_0 of both atoms. Movement of the atom in any direction from position r_0 induces generation of the forces which counteract with a displacement. Macroscopic deformation of the crystal is thus caused by change of interatomic distances in the same direction.

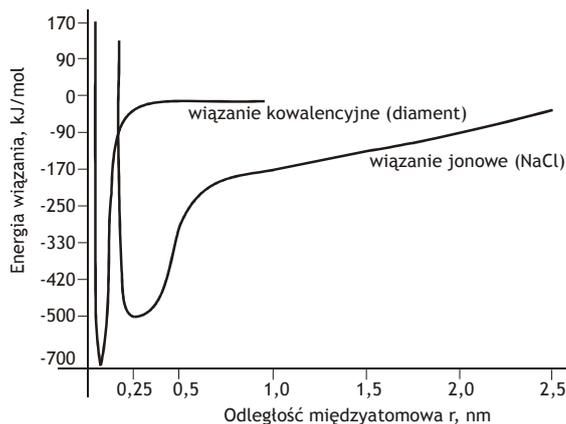


Fig. 3. Energetic models of formation of ionic and covalent bonds

Energies and forces occurring between atoms forming particular kinds of bonds may be presented using energetic model. Fig. 3 presents energetic model of formation of ionic and covalent bond. Energetic model of metallic bond is similar to the one of covalent bond.

Character of variability of potential function is related to the bond kind. The stronger is the bond, the deeper and narrower is a well of potential energy. Particular energy increase in case of crystal with stronger bonds causes smaller change of its dimensions.

Mechanical strength

Mechanical strength in general is an ability of the materials to withstand a load without failing. It is expressed in terms of force or stress which causes loss of material cohesion and its rupture into two or more pieces.

Significant feature of all ceramic materials at ambient, moderate and partially also elevated temperatures is their brittleness. Brittle failure is the one in which material undergo decohesion without occurrence of significant strains before. It is illustrated by the line OF in Fig.1. Brittle failure differs from plastic failure, typical for many metals, where decohesion occurs at much higher strains (OAF curve in Fig.1). In case of ductile polycrystalline metals with face-centered cubic structure the plastic failure is a result of reduction of the material cross-section due to its plastic deformation (Fig. 4). An ability of a material to withstand brittle failure is called ductility or fracture toughness.

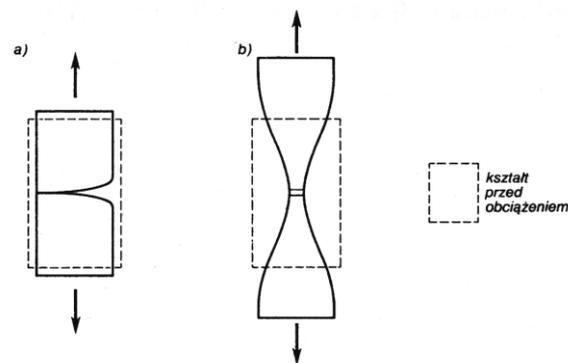


Fig.4. Scheme of elastic strain formation (a) and plastic strain formation (b)

Second typical feature of the ceramic materials is a considerable difference of the strength at different state of stress. It may be generally accepted, that for the ceramic materials tensile strength is the lowest one. Bending strength is up to three times higher, and compression strength is even fifteen times higher.

Reference point for evaluation of fracture toughness of the materials is a tensile strength of interatomic bonds which is called **maximal** or **theoretical strength** σ_m . It may be stated, that work performed by the load is consumed by formation of two new surfaces, each possessing an excessive surface energy γ . The bond ruptures when:

$$\sigma_m = \sqrt{\frac{E\gamma}{r_0}} \quad (4)$$

Equation 4 is often used for calculation of theoretical strength from measurable values of E , γ and r_0 . However, it should be remembered that crystals consist of many atoms and bonds, which interactions have to be taken into account.

Table 1.

Material type	Theoretical strength [GPa]	Whiskers strength [GPa]	Strength of bulk polycrystals [GPa]
α -Al ₂ O ₃	53	14-23	0.5-1.3
β -SiC	122	7-35	0.3-0.6
graphite C	122 (ll to a axis)	20-25	<0.5
WC-Co			2.1-2.5

Besides generally higher theoretical strength of ceramic materials comparing to metals it is worth to note, that in case of currently fabricated materials real values of the strength close to the theoretical one are achieved only in case of whiskers (monocrystalline fibers) and are slightly lower in case of polycrystalline fibres. The fibers are characterized by relatively flawless structure and structure of whiskers is almost perfect, without any discontinuities. Mechanical strengths achieved in case of typical, bulky polycrystals are two to three times lower than the theoretical values, which is caused by defects (slits, micro-cracks, etc.).

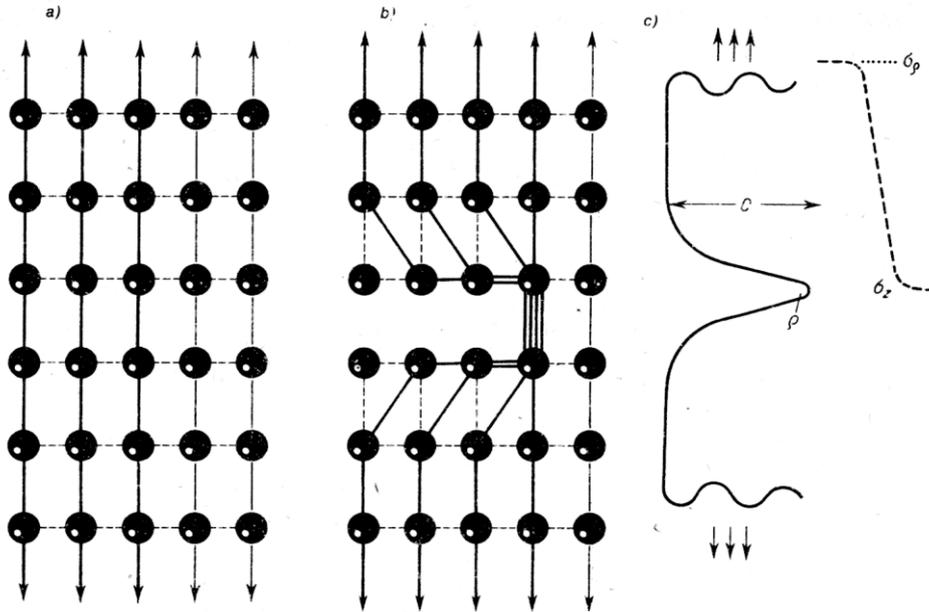


Fig.5. Diagram showing formation of stresses at pore tip

In the situation presented in Fig.5 transfer of an external load along two broken chains of atoms becomes impossible, and it has to be carried out via different path i.e. round the pore. Chain of atoms on the pore tip transfers four times larger load that in case of a model without the pore, and also stresses in this place are four times larger than expected from the average external loads. It means that in this case a stress concentration occurs. Only at higher distance from the pore surface stresses are lower and equal to the external load, $\sigma_z = P$ (Fig.5). Accurate values of the coefficient of stress concentration, i.e. number which states how many times a local stress close to the pore surface is higher than the average stress far from the pore (the external load) can be calculated using Inglis' equation:

$$\sigma_\rho = \sigma_z \left(1 + 2\sqrt{\frac{c}{\rho}} \right) \approx 2\sigma_z \sqrt{\frac{c}{\rho}} \quad (5)$$

Internal stresses close to the slit tip (crack tip) are a multiple of the exerted external loads P , and may there achieve value equal to the theoretical strength of bond σ_m at moderate external loads P (Fig. 5). In such conditions it may be expected, that cracks which already exist in the material subjected will propagate. Combining equations 4 and 5 one will obtain:

$$\sqrt{\frac{E\gamma}{r_0}} = 2\sigma_z \sqrt{\frac{c}{\rho}} \quad \text{stad} \quad P = \sigma_z = \sqrt{\frac{E\gamma\rho}{4cr_0}} \quad (6)$$

The so far considerations may be concluded, that even at low loadings it is difficult to avoid formation and/or development of critical cracks in the material. That is why a ductility (fracture toughness) of the material is so important factor. In fact it is a measure of energy absorbed by the material during development of the cracks. The higher the energy is, the higher is a work which must be performed by the external loads to break the material. **Primary parameters describing ductility** of the material are K_c and γ_c . Brittle rupture may occur at three different modes of the material deformation, presented in Fig.6, or their combinations. The highest stress concentration takes place when fracture occurs in mode I.

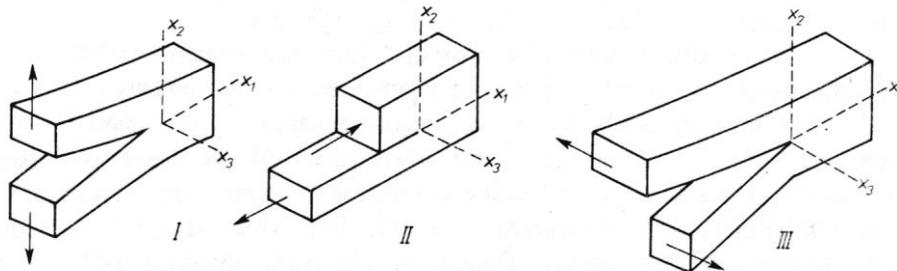


Fig.6. Primary modes of brittle rupture (failure)

In other words, during flat state of straining in mode I the risk of brittle failure is higher than that in case of the modes II and III. That's why, aiming the determination of the lower limit of fracture toughness, the analysis of the material straining may be restricted to the mode I.

Fracture toughness. Griffith's theory

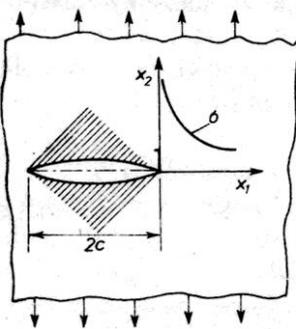


Fig.7 Griffith's crack and stresses (σ) in the material subjected to tensile loads

Loading a thin plate, containing in its centre an infinitely thin elliptical crack (Griffith's crack, Fig.7) perpendicular to the equatorial axis, leads, due to elastic strains, to accumulation of elastic energy in the material, which magnitude at the unit length is w . At the same time two boundary surfaces of the crack move apart in direction of the polar axis. Loss of cohesion of the material in a region of the crack enables free changes of the material volume without obstacles from elastic constraints related to existence of continuous system of interatomic bonds. As a result, part of elastic strain energy accumulated in that region (shaded at Fig.7), w_R , may be discharged.

Elastic strain energy stored in the material, in respect to the unit length, is thus $w - w_R$, where w – elastic strain energy of the material without the crack. At the same time, decohesion of the material leads to formation of two new solid-gas (or vacuum) division surfaces at the crack length with an excessive energy γ . In case of a crack having length equal to $2c$ along the equatorial axis it is accompanied by energy absorption, $G=4\gamma c$. The crack may increase its dimensions along the

equatorial axis, i.e. propagate in the material, only if at every stage of this process the energy decreases. Fig. 8 presents changes in the system total energy dU vs. increment of the crack length dc . Because $G = f(c)$ and $w_R = f(c^2)$, stronger changes of w_R with the cracks length than in case of G may be expected.

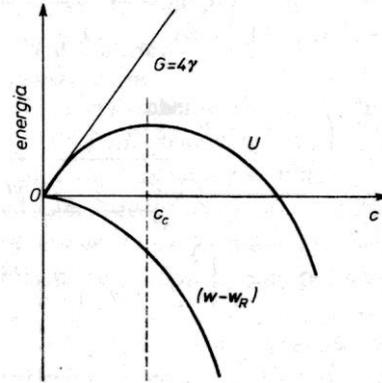


Fig.8 Changes of total energy (U), surface energy, and elastic strain energy stored in the material ($w-w_R$) vs. length of the Griffith's crack , c

Necessary condition of self-propagation of the crack under a given load is formation of crack with critical (half) length c_c , above which system energy decreases with increasing length of the crack. Relationship between the critical load, above which the crack starts to propagate may be presented as follows:

$$P_c = \sigma_{z,c} = \sqrt{\frac{2\gamma E}{\pi c_c}} \quad (7)$$

E and γ are both material constants, so critical length of the crack depends of the load applied – the higher the external load is, the smaller cracks may cause catastrophic failure of the material. In case of application where a load is equal to the theoretical strength of bonds the c_c equals approximately three times the equilibrium length r_0 .

Relation (7) is right for a crack located inside of the material. In case of crack placed on the materials' surface the stress concentration at the crack tip is higher. Because of that, dimensionless coefficient Y is introduced, which value depends of location of the crack within the material. Moreover, the stress concentration strongly depends of the crack geometry. It decreases when approaching rounded shape. On the basis of those considerations dimensionless coefficient Z is introduced, which enables to generalize relation (7) for different cases than the flat Griffiths crack. Generalization of equation (7) is:

$$P_c = \sigma_{z,c} = \frac{Z}{Y} \sqrt{\frac{2\gamma E}{\pi c_c}} \quad (8)$$

Strength of real ceramic materials is generally higher than the one expected from relation (8). It implies, that the real materials don't behave like ideally elastic solids, which were described by the Griffiths theory. This fact has many causes. One of them may be local plastic deformation of the material close to the crack tip, the other may be branching of cracks, mainly related to presence of weaker intergranular and interphase boundaries. One of the most important factors determining strength and toughness of the materials is state of their surface. In a perfect form it occurs in case of

high-quality glasses, which don't contain any coarse defects inside. **The phenomena listed above are deliberately used for increasing the fracture toughness of ceramic materials and strength.**

It should be stated, that the surface energy γ in equation (7) should be replaced by an effective surface energy, or better an energy of fracture γ_{ef} :

$$\gamma_{ef} = \gamma + \gamma_{pl} + \gamma_r + \gamma_m + \gamma_{pf} + \gamma_i + \dots + \gamma_k \quad (9)$$

where:

γ - specific surface energy,

γ_{pl} - energy dissipated at local plastic deformations

γ_r - energy dissipated due to branching of cracks or formation of micro cracks

γ_{pp} - energy absorbed due to occurring phase transformations (polymorphic transformations)

$\gamma_m, \gamma_i, \dots, \gamma_k$ - other causes increasing γ_{ef} .

In case of e.g. fiber reinforced composites the "other causes" is energy necessary to pull out fibers from the matrix.

Coming out from equation (7), in which $\gamma = \gamma_{ef}$, the material constant which characterizes the material resistance toward catastrophic propagation of an unstable crack may be derived. Multiplication of both sides of equation (7) by $\sqrt{\pi c_c}$ leads for the flat stress state to:

$$\sigma_{z,c} \sqrt{\pi c_c} = \frac{Z}{Y} \sqrt{2E\gamma_{ef}} = const \quad (8)$$

It means, that in case of initiation of propagation of unstable crack able to penetrate through the material a product of $\sigma_{z,c}$ and $\sqrt{\pi c_c}$ is a constant, which depends only of E , γ_{ef} and Z , Y .

Besides the effective fracture energy, other criterion of the material resistance to the fracture may be derived basing on macroscopic approach of Irwin and William, which defines relations between permissible load and length of the critical crack. In that respect, Irwin modified Griffith's approach (energy balance) introducing concept of a force causing propagation of the crack with a unit length, and he formulated a new criterion of initiation of uncontrolled crack propagation. It occurs when at the crack tip critical value of the stress concentration is reached. **Parameter K_I** (for I mode of cracking) is called a coefficient of stress concentration. In turn, **K_{Ic} coefficient** is defined as **the fracture toughness. The essence of the concept of the fracture toughness is, that K_I coefficient describing change of stress distribution in the elastic material in presence of a crack and it reaches its maximum value K_{Ic} when catastrophic crack propagation in the material is initiated.** K_{Ic} coefficient shouldn't be mixed up with the coefficient of stress concentration, because, similarly to γ_{ef} , **it is a material constant.** Irwin found following relation of both constants:

$$K_c^2 = E\gamma_{ef} \quad \text{dla PSN} \quad (9)$$

$$K_c^2 = \frac{E\gamma_{ef}}{1-\nu^2} \quad \text{dla PSO}$$

For the flat stress state (PSN) considered by Griffith it may be written as follows:

$$K_c = \sigma_{z,c} \sqrt{\pi c_c} = \sqrt{E\gamma_{ef}} \quad (10)$$

Exemplary K_{Ic} and γ_{ef} values for various materials are gathered in Table 2.

Table 2. Selected mechanical and elastic properties of various materials

Material	Hardness HV [GPa]	Yield stress R_e [GPa]	Young's modulus [GPa]	Fracture toughness [$\text{MPa m}^{0,5}$]
$\alpha\text{-Al}_2\text{O}_3$	14-18	5	360-390	3,4-5,6
$\text{Al}_2\text{O}_3+20\% \text{ZrO}_2$ (particulate composite)				6,5-8
CZP (cubic) ZrO_2	10-12	3	160-220	3,8-5
TZP (tetragonal) ZrO_2 (12% mol CeO_2)				10-15
Na-Ca glass	5,8	1,9	70	0,6
$\beta\text{-SiC}$	18-25	7	340-450	3-4,5
$\text{SiC(w)}\text{-Al}_2\text{O}_3\text{(o)}$ (fibrous composite)				21
$\alpha\text{-Si}_3\text{N}_4$				5,5
diamond	81	27	1000	5,3
$\text{WC-Co}^{*)}$	12-20	5	540-610	7-28
Ti_3SiC_2 (nano-laminate)				7-8
Cu	0,1-0,8	0,06	124	100
Al	0,1-0,4	0,04	69	350
constructional steel	1,6-5,0	0,3-2,0	190-210	150
PMMA (Plexiglas)	0,16	0,06-0,11	3,4	0,9-1,4

The effective surface energy is in fact the effective fracture energy. Occurrence of phenomena, which contribute to the effective fracture energy is facilitated by properly designed microstructure of the material. Main types of microstructure are shown in Fig.9.

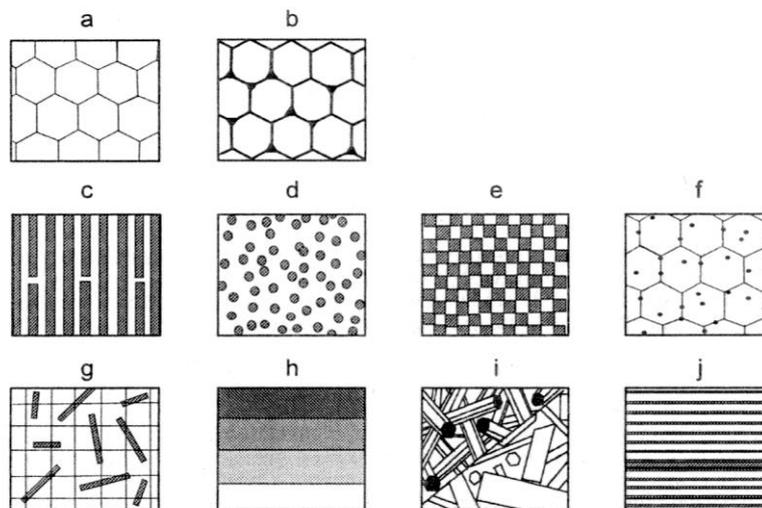


Fig.9. Schemes of microstructures of various ceramic materials: a), b) polycrystals, c) fiber reinforced composites, d) particulate composites, e) materials with duplex microstructure, f) materials containing nanometric particles of the other phase, g) materials containing short fibers of the other phase, h) laminates, i) materials with elongated grains, j) nano-laminates.

Hardness

Hardness may be defined as resistance of a material to the permanent (plastic) deformation caused an indenter forced in. Ceramic materials such as corundum (Al_2O_3) carborundum (SiC) and diamond (C) belong to the hardest solids. Almost all other materials may be cut with them, also their powders are used as grinding and polishing media. A hardness of those materials comparing to that of some metals (Table 2) clearly indicates predominance of the former ones. This is due to the nature of chemical bonds and its influence of movement of dislocations in ceramics and metals. During the

plastic deformation in hardness test dislocations existing in the material slip, so such test principally determine ease of moving dislocations in the material. In case of metals that ease is relatively high, because moving dislocation displaces atoms bonded with rather weak metallic bond. Energy of this bond comes from electrostatic interaction between positive charged atomic cores and negatively charged "electron gas". Such bonds are delocalised. Ceramic materials exhibit different properties. Due to covalent bonds (diamond, carborundum) or ionic-covalent (corundum) their crystalline network put up a strong resistance to the dislocations movement. In case of localized covalent bonds it is necessary to break them and subsequent reproduce them. In case of ionic bonds, dislocation slip is easier, but it may take place mainly in such crystallographic directions in which attraction between anions and cations occurs. This reduces number of slip systems necessary to move dislocations in ionic polycrystals and is a cause of their relatively high hardness. Rightness of this reasoning is confirmed on the basis of comparison between metals yield stress (R_e) with hypothetical yield stress for ceramics (Table 2). Such estimated R_e values for ceramic materials are even one order of magnitude higher than those of metals. It is worth to emphasise, that similarly to hardness, also Young's modulus of metals and ceramics distinctly depends of the atomic bond nature (Table 2). Those relationships are more complex in case of polymers. If we limit our considerations only to examples of selected constructive polymeric materials, which are brittle at room temperature, such as hardened epoxy or polyester resins and polymethyl methacrylate (PMMA, Plexiglas), it may seem that their Young's modulus and hardness are determined by strong covalent carbon-carbon bonds forming main polymeric chain. It means, that such polymers should have mechanical properties similar to those of diamond. But besides the strong C-C bonds there are there also weak, secondary bonds between the chains. Their presence determines in fact relatively high deformations under loads, and thus low hardness and Young's modulus.

As it was stated above, estimated values of yield stress of ceramic materials are much higher than those of metals. However, contrary to metals, **ceramics will break under tensile load reaching yield stress**. That's why the estimated values of R_e for ceramic polycrystals (Table 2) have only comparative meaning. **It is caused by their low fracture toughness (K_{Ic})**. For the same reasons the cracks are easily formed inside ceramics by a sharp indenter during hardness test. Threshold value of a loading force P^* which leads to the material cracking may be determined. It is a very good measure of the material cleavage. P^* force values are useful in a process of designing of ceramic materials. If during operational use of a product acting forces are lower than P^* they won't cause cracking but only deformations, which may be lowered by increasing the material hardness.

In opposite situation propagation of cracks will take place, which can be prevented by increasing the fracture toughness for example by introduction to the material particles which may hinder the cracks (ide of the composites).

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