NASA TECHNICAL MEMORANDUM NASA TM-77504

BRITTLENESS OF CERAMICS

F. Kroupa

(NASA-TM-77504) BRITTLENESS OF CERAMICS N85-12156
(National Aeronautics and Space
Administration) 46 p HC A03/MF A01 CSCL 11F
Unclas
G3/27 11241

Translatior of "Krehkost keramiky," Ceskoslovensky casopis pro fyziku, Section A, Vol. 32, No. 1, 1982, pp 1-25.

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D.C. 20546 AUGUST 1984

STANDARD TITLE PAGE

1. Report No. NASA TM- 77504	2. Government Accession No.	3. Recipient's Catalog No.

4. Title and Subtitle
BRITTLENESS OF CERAMICS

5. Report Date
August 1984

6. Performing Organization Code

7. Author(s)
Frantisek Kroupa

8. Performing Organization Report No.

10. Work Unit No.

9. Performing Organization Name and Address
Leo Kanner Associates
Redwood City, California 94063

11. Contract or Grant No.
NASw- 3541

13. Type of Report and Period Covered
Translation

12. Sponsoring Agency Name and Address
National Aeronautics and Space Administration, Washington, D.C. 20546

14. Sponsoring Agency Code

15. Supplementary Notes

Translation of "Krehkost keramiky," Ceskoslovensky casopis pro fyziku, Section A, Vol. 32, No. 1, 1982, pp 1-25.
(A82-28297)

16. Abstract

The main characteristics of mechanical properties of ceramics are summarized and the causes of their brittleness, especially the limited mobility of dislocations, are discussed. The possibility of improving the fracture toughness of ceramics and the basic research needs relating to technology, structure and mechanical properties of ceramics are stressed in connection with their possible applications in engineering at high temperature.

17. Key Words (Selected by Author(s))

18. Distribution Statement
Unlimited-Unclassified

19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 45	22.

TABLE OF CONTENTS

1. Introduction p 2
2. Definition of Ceramics p 3
3. Remarks on Structure and Selected Physical Properties p 3
4. Elastic Properties, Ideal and Actual Strength p 4
5. Plastic Deformation of Ceramics p 6
    - 5.1 Mechanisms of Plastic Deformation of Crystalline Substances p 6
    - 5.2 Properties of Dislocations in Ion and Covalent Crystals p 6
        - 5.2.1 NaCl type Ion Crystals p 6
        - 5.2.2 Other Types of Ion Crystals p 9
        - 5.2.3 Covalent Crystals p 10
    - 5.3 Plastic Deformation of Polycrystalline Ceramics p 11
        - 5.3.1 Propagation of Creep Across Grain Boundaries p 11
        - 5.3.2 Number of Independent Creep Systems, von Mises' Criterion and Maneuverability of Dislocations p 12
        - 5.3.3 Strength of Grain Boundaries p 13
        - 5.3.4 Macroscopic Plastic Deformation p 14
    - 5.4 Creep of Ceramics p 15
    - 5.5 Summary of Causes for Limited Workability of Ceramics p 15
6. Occurrence and Propagation of Cracks p 16
    - 6.1 Measure of Brittleness p 16
    - 6.2 Fracture in Monocrystals p 17
        - 6.2.1 Nucleation of Cracks p 17
        - 6.2.2 Propagation of Cracks p 17
    - 6.3 Fracture in Polycrystalline Ceramics p 18
    - 6.4 Concluding Remarks on the Brittleness of Ceramics p 19
7. Potential for Improving the Mechanical Properties of Ceramics p 19
    - 7.1 Strength Improvement p 19
    - 7.2 Ceramics in Composite Materials p 21
8. Contemporary Technical Approach to Brittleness of Ceramics p 21
9. Conclusion p 24

References p 25

BRITTLENESS OF CERAMICS

Frantisek Kroupa
State Research Institute for Materials, Prague

Key findings about the mechanical properties of ceramic materials are summarized and the causes of their brittleness, particularly the limited mobility and maneuverability of dislocations are discussed. The article also points out the potential for increasing the resistance of ceramics against fracture and the need for additional basic research in the technology, structure and mechanical properties of ceramics in connection with its prospective application in general engineering for parts exposed to high temperatures. /1*

1. Introduction /2

The typical mechanical property of contemporary ceramics is its brittleness: for all practical purposes, ceramics is not capable of plastic deformation and is subject to damage by brittle fracture, i.e., rapid unstable cleavage fracture with low absorption of energy. Thus it lacks properties that are typical of metals, workability (capacity for considerable plastic deformation) and toughness (strong absorption of energy during sustaining of damage).

However, workability and the types of damage it can produce are not some absolute, invariable properties of a certain class of materials. Workability depends not only on the material's composition and structure, but also on their failure mechanisms and on external conditions, e.g., the type and rate of stress exposure and, particularly, on temperature. This fact has been known about metals for millenia and led also to the proverb "Strike the iron while it is hot."

---

*Numbers in the margin indicate pagination in the foreign text.

The malleability of some high-strength steels at low temperatures is so low that they are subject to damage by brittle fracture. It is even possible to prepare metallic materials as brittle as ceramics: all it takes is poor steel quenching. On the other hand, efforts to prepare high-strength ceramics have met with little success for the time being and ceramics remains brittle even at considerably high temperatures.

Power engineering has been developing over the past several years efforts toward increasing operational temperatures that would lead to improved effectiveness of power engineering systems. Use of metals constitutes in this respect a serious obstacle to continued technical progress: even the best of special alloys can withstand long-term exposure only up to temperatures of some 1100°C: they become subject to fast corrosion and sustain damage through creep. Thus, technology turned its attention to ceramic materials with a high melting point and excellent resistance to chemicals. Intensive research is currently conducted in many countries into the mechanical properties of ceramic materials with the objective of improving them and decreasing the danger posed by brittle fracture so that ceramics could be used for components exposed to high stress.

This objective represents one of the most difficult, but also one of the most significant goals of material research in this century. It calls for solution of an entire series of scientific problems from the area of physicochemical processes in the production of ceramics that determine its structure, and of microphysical processes occurring during its exposure to stress [1].

We shall attempt to clarify in this article what causes ceramics to be brittle and what approaches are being considered toward an either substantial or at least a modest improvement in the mechanical properties of ceramic materials. Herein we must devote our attention to two processes which occur simultaneously during exposure to stress and mutually affect each other and as they duel, even a small unilateral superiority could produce a basic change in the nature of fractures. This involves, on the one hand, plastic deformation due to mobility of dislocations and, on the other hand, occurrence and propagation of sharp-edged /3 cracks. Let us first examine these processes in monocrystals of substances of which ceramics is composed and, subsequently, significant changes occurring in these processes in polycrystalline ceramics.

2. Definition of Ceramics

The definition of ceramic materials (also referred to briefly as ceramics) is far from unequivocal. The original narrower meaning is derived from the Greek kerannimi (I mix, I blend--e.g., wine, clay) and keramos--a product originated through mixing; the meaning became narrowed down to products made of clay. To this corresponds the traditional definition of ceramics as inorganic non-metallic materials prepared from an initial powdery raw material with the use of heat (e.g., by drying, sintering, etc.).

The more general modern definition does away with the specificity of technology and defines ceramics as a material the main component of which is constituted by inorganic compounds of non-metallic nature [2]. This definition includes not only "traditional" ceramics (porcelain, cement, bricks), but also abrasive materials and many of the so-called "new" ceramic substances, such as oxidic ceramics (Al_2O_3, ZrO_2, ThO_2, BeO, MgO, UO_2), ferrites, ferroelectrica, nitrides, carbides, borides, etc. New ceramics is characterized by the fact that it is produced from relatively pure raw materials and often from pure initial chemicals such as synthetic ceramics. Increased care in ceramic method of production is devoted to its sintering (in vacuum, in protective armosphere, at higher temperature, under pressure, etc.), so that the relative volume of pores becomes diminished and improves the cohesion of grains.

While most substances included among ceramics are crystalline substances, traditional ceramics (e.g., porcelain, glazes) also contains a considerable part of vitreous phase. According to the general definition in Englisg literature, even glasses are added to ceramic materials, but this article shall be limited to crystalline ceramics.

3. Remarks on Structure and Selected Physical Properties

Ceramic substances are bonded by ionic and covalent interatomic bonds. However, their bond is not purely ionic (such as in KCl) nor purely covalent (such as in, e.g., a diamond), both types tend to appear as a rule. The prevalent type of bond becomes conspicuously manifested in all physical properties, e.g., not only in electric and optical properties, but also in mechanical properties. Crystalline structures of compounds forming the basis of ceramic substances are already known for their most part with prevalence of complex cubic and hexagonal lattices [2]. Of basic importance from the viewpoint of technology and properties of ceramics is knowledge of phase diagrams and phase transformations of crystalline ceramic substances and glasses. Of prime importance to traditional ceramics from binary systems are Al_2O_3-SiO_2, MgO-SiO_2 and MgO-Al_2O_3, from ternary MgO-SiO_2-Al_2O_3. The number of thoroughly researched systems is great, e.g., [3] lists over 5000 binary and ternary phase diagrams. Ceramic materials usually have a complex microstructure: they are formed from crystalline grains of various shapes and sizes and of varying chemical composition, of many intermediate phases on grain boundaries and of pores of various shapes and sizes distributed both between and inside the grains [2].

We shall offer several comments on the physical (particularly thermal) properties of ceramics from the viewpoint of their relation to mechanical properties--which will be dealt with in subsequent chapters.

In addition to specific weight Q defined as weight of a unit of volume of a given substance, in the case of ceramics is introduced also volume weight Q_v as the weight of unit volume of ceramic materials containg pores. From these magnitudes it is then possible to compute the porosity of ceramics [i.e., the relative volume of pores $P = (Q - Q_v)/Q$] which is characteristic of ceramics. When porosity drops below 5% the ceramics becomes, as a rule, impermeable to gases and thus vacuum tight. The volume weight of ceramics tends to range between 2500-3500 kg/m^3, i.e., approximately identical to aluminum alloys. /4

Ceramics does not differ any too greatly from metals in regard to specific heat. Even thermal expansivity α is on the same order. Thermal expansivity in monocrystals is given by the symmetric tensor of the second order α_{ij}; it is isotropic only in cubic crystals [4]. In thermal treatment of polycrystalline ceramics the anisotropy of thermal expansivity of non-cubic crystals is one of the causes of internal stresses. Internal stresses can occur also during changes in the temperature of polycrystalline materials composed of more phases with varying thermal expansivity. These can lead in ceramics to occurrence of intercrystalline fractures, either directly or in combination with external stress, because, contrary to metals, it cannot easily relax stresses by plastic deformation. Low thermal conductivity λ is one of the most significant properties of ceramics in its traditional applications as thermal insulators. However, inadequate thermal conductivity detrimentally affects mechanical properties. At given marginal and initial conditions, heat distribution depends on specific thermal conductivity $a_T = \lambda/(QC_p)$ and its extent together with expansivity α and elastic constants codetermines the occurrence of thermal stresses during heat surges. A high a_T offers the advantages of lowering these stresses; However, in comparison with metals, heat conductance a_T of ceramics is also lower by an order or so due to low thermal conductivity λ (specific weight Q and specific heat C_p is of the same order in both metals and ceramics).

The contemporary mechanical properties of ceramins are for the most part suitable for applications in electrotechnical engineering where electric and magnetic properties are of prime importance, nevertheless an improvement in tensile strength and, particularly, in resistance against mechanical and thermal impacts would be most welcome.

A typical optical property of inorganic non-metallic materials in the form of monocrystals or glasses is good transmittance in the region of visible and near infrared radiation. However, polycrystalline ceramics is composed of particles with varying refractive indices and of pores. Scattering of light and multiple reflections render ordinary ceramics non-transparent and account for its typical milky coloring, in the case of uneven surfaces (ceramics without glazing) the diffusion reflection gives it a matte appearance. However, already in current production is now oxidic ceramics (made of, e.g., pure Al_2O_3 , MgO and BeO) that contains so few pores (less than 0.5%) as to be translucent or even transparent. Its mechanical properties make it superior to glasses for use at high temperatures.

4. Elastic Properties, Ideal and Actual Strength

Polycrystalline ceramic substances are elastically isotropic and, as such, can be characterized by two independent elastic constants, e.g., the modulus of elasticity in tension E and by the Poisson's constant ν (which is rarely used). Dependence of the modulus of elasticity on porosity P is nonlinear and is given in approximation by MacKenzie's relation [2], $E = E_0 (1 - 1.9P + 0.9 P^2)$. At porosity $P = 0.5$ the modulus of elasticity would drop to as little as one-fourth; porosity leads to a decrease in the modulus of elasticity. Moduli of elasticity in tension of some ceramic materials with low porosity are shown in Table 1; they are on the same or higher order than those of metallic materials.

Table 1. Modulus of Elasticity in Tension E and Orientational Value of Bending Stregth R_0 of Selected Ceramic Materials at Room Temperature (according to [2]).

Material	GPa	MPa
Al_2O_3 - sintered corundum	380	(200 - 350)
BeO	310	(140 - 280)
B_4C	290	350
MgO	210	100
ZrO_2	150	80
$MgAl_2O_4$ - sintered spinel	240	90
SiC	400	170
SiC - sintered under pressure	400	700
Si_3N_4	220	170
Si_3N_4 - sintered under pressure	310	800
Porcelain	70	(30 - 50)
Magnesite brick	170	30
Fireclay brick	100	5

Ideal tensile strength R_{id} of ionic and covalent crystals which form the basis of ceramic materials is on the order of $E/10 \pm 50\%$. Ideal strength, in which ceramics is superior to metals, is approached by thin monocrystalline fibers and for that reason ceramic fibers (particularly fibers of oxides, nitrides and carbides) are regarded to be very viable reinforcing fibers for use in many composite substances [5]. A study [6] even envisions that practical applications in the future will be found by compo- /5
nents made of macroscopic monocrystals of some ceramic substances with strength of 10 to 100 GPa.

Ideal strength is given by the properties of a perfect lattice. From among mechanical properties of real materials only elastic properties belong among those that are principally constituted by the properties of a perfect lattice and are affected only slightly by presence of disturbances in the latter. On the other hand, all nonelastic mechanical properties, e.g., yield point and ultimate strength, are determined by structural disturbances, particularly by dislocations (in workable materials) and cracks (in brittle materials).

While yield point and strength are easily reproducible in workable materials and can be regarded as material properties, tensile strength is not reproducible in conspicuously brittle materials and it cannot be regarded as a material constant. The reason is that it depends on the size of cracks which is difficult to control and on the material property determining the material's resistance against propagation of cracks. Measuring of the tensile strength of brittle ceramic materials would lead to a great dispersion in measured values and, consequently, tensile strength is not quoted for ceramics as a rule. Even bending strength cannot be considered in the case of ceramics to be a purely material constant (it also depends on the size of surface cracks), nevertheless the dispersion of measured values is smaller. For the sake of orientation, Table 1 lists bending strengths measured at room temperature. They are lower by approximately three orders than the modulus of elasticity in tension and, thus, lower by two orders than ideal strength. These bending strengths are reduced by another order of one during long-term exposure to stress under operational conditions. Conversely, compression strength is substantially higher in ceramic materials and is more easily reproducible, because it is less affected by surface cracks.

The starting point for a more detailed explanation of the mechanical properties of ceramics--such as lack of workability, brittleness and limited long-term strength--must be the nature of distubances in the structure of ceramics. These problems will be dealt with in the subsequent chapters.

5. Plastic Deformation of Ceramics

/6

5.1 Mechanisms of Plastic Deformation in Crystalline Substances

The workability of crystalline substances is determined almost exclusively by their capacity for creep mobility of dislocations under exposure to shearing stress. Plastic deformation is only exceptionally abetted by other processes, such as twinning and phase transformations caused by stress. Plastic deformation in polycrystalline materials is promoted at high temperatures also by slippage along grain boundaries and by diffusion creep.

Easy workability of metals has to do with two properties of dislocations in a metallic crystalline lattice:

a) their Peierls-Nabarr (PN) stress is low and, consequently, their mobility in slip plane is essentially good,

b) their number of creep systems is high, dislocations can easily intersect and helical dislocations can avoid obstacles by transverse creep. This set of properties endows dislocations with maneuverability in developing of plastic deformation under more complicated conditions (when mere mobility of dislocations along one or several creep planes is not enough); this is what is called the maneuverability of dislocations.

The more difficult workability of ceramic materials has to do primarily with lower mobility or maneuverability of dislocations in lattices with an ionic or covalent bond.

Let us point out that in the case of traditional ceramics in particular there are many secondary causes which make any manifestation of workability impossible by leading to brittle fracture even at very low tensile stress. It is particularly their extraordinary inhomogeneity of structure, imperfect adhesion of grains, porosity, prevalence of surface cracks, presence of the vitreous phase, existence of internal stresses, etc. Nevertheless, these causes are not considered to constitute the principial limitation of workability: they have been eliminated to a considerable extent in new ceramics, yet the latter still can become subject to damage by brittle fracture, even though at somewhat higher stress exposures.

Therefore, let us first examine the main causes, i.e., the properties of dislocations in monocrystals and their manifestations in polycrystalline ceramics and, subsequently, also the important role of the strength of grain boundaries.

5.2 Properties of Dislocations in Ionic and Covalent Crystals

5.2.1 NaCl Type Ionic Crystals

This cubic lattice, in which crystallizes also the significant ceramic substance MgO can be imagined as composed of two cubic sublattices centered in a plane containing cations *A* and anions *B* (see Figure 1). Burgers' vectors of dislocations $b = (\frac{1}{2})$ <110> determine the directions of creep of which there is a total of six. The creep surface could be constituted from the geometrical viewpoint by a general cylindrical surface with a generatrix in direction <110>; during creep along this surface occurs mutual mobility of "rods" of ions of identical charge in the most densely occupied directions. Selection of the creep plane is affected by the fact that during creep along the most densely occupied planes {001} are formed intermediate configurations with relatively considerable energy and, thus, the PN stress of dislocations along these planes is relatively high. The lowest PN stress in dislocations occurs during creep along planes $\{1\bar{1}0\}$: all extant experiments confirm that these are the basic creep planes of all crystals of the NaCl type. However, there is only one such creep plane for each Burgers' vector, making helical /7 dislocations incapable of transverse creep in the basic system.

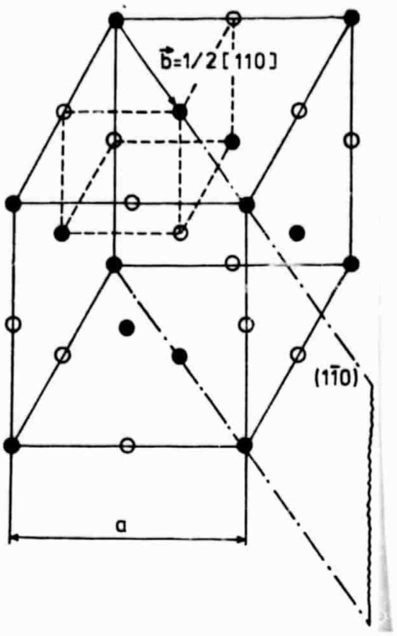

Figure 1. NaCl Type Lattice

However, the PN stress on planes {001} decreases with increasing temperature faster than on {1$\bar{1}$0} planes. At a certain temperature $_1$ these stresses are identical (Table 2). Thus is added a secondary creep system and helical dislocations now can deviate in transverse creep.

Table 2. Temperatures T_1 at Which PN Stress Decreases in {001} Planes to PN Values of {1$\bar{1}$0} Planes.

Crystal	T_1 [K]	T_1/T_0
AgCl	170	0.2
NaCl	670	0.6
LiF	700	0.6
MgO	2000	0.7

The basic creep system cannot mediate plastic deformation in tension or compression of monocrystals at a special orientation of axis <111>; in all six planes {1$\bar{1}$0} there namely occurs in this case shearing stress in the direction of creep <110> zero. The crystal then has two possibilities: either brittle fracture or forced creep along the secondary creep system, i.e., along planes {001}.

NaCl type monocrystals are capable of plastic deformation, at least in the basic creep system, already at the lowest temperatures. Curves of compressive stress--deformations for MgO mono- /8
crystals at various orientations and varying temperatures--are shown in Figure 2. At axis orientation [100] a 5% permanent contraction is obtained at a temperature of -196 °C, a more significant permanent contraction is obtained at orientation [111] only beyond 300°C, in polycrystalline material only above 1000°C.

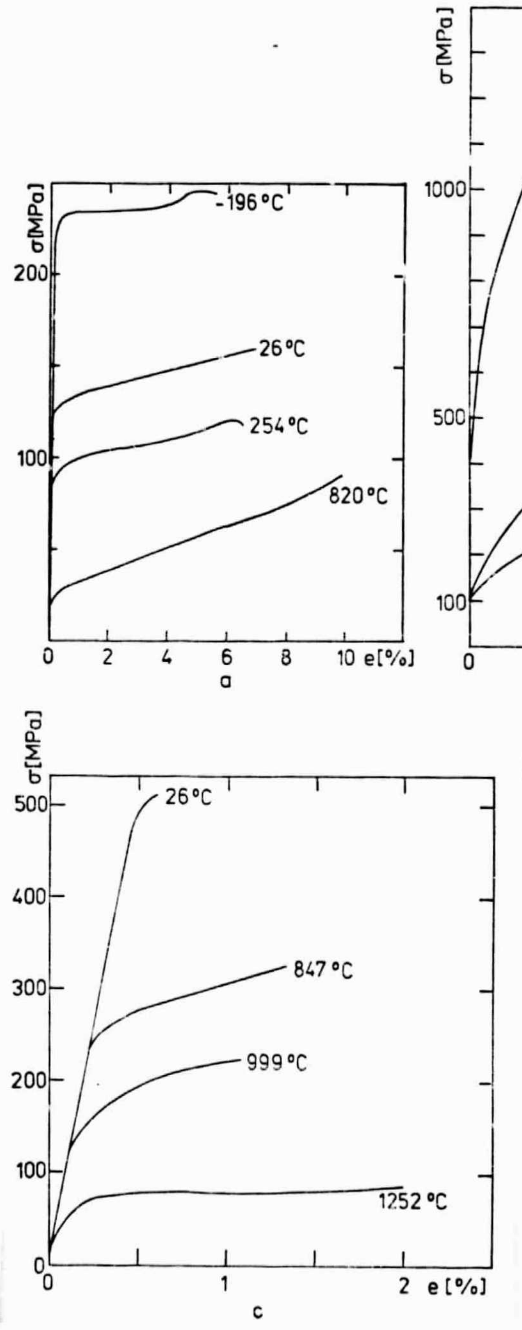

Figure 2. Stress curve for Exposure of MgO Crystals to Compression at Various Temperatures:
a) axis of sample [100];
b) axis of sample [111];
polycrystalline material (acc. to [9]);
deformation velocity $\dot{e} \approx 10^{-4}\ s^{-1}$.

In the case of ionic crystals, preference is given to uniaxial /9 compression tests, because during tensile strength tests under temperature T_1 there occurs sudden fracture resulting in a wide dispersion of the attained permanent elongation. Thus, maximum permanent deformation during exposure to compression stress is a more suitable measure of workability.

Under temperature T_1 which we introduced as the temperature at which secondary creep systems function as easily as the basic system, despite easy mobility of dislocations in the basic system there are encountered certain difficulties during development of plastic deformation. During exposure to compression these difficulties occur only during a single orientation of the compression axis, however, during exposure to tensile deformation during all orientations, because crystals, as a rule, contain cracks; under the conditions prevalent at the face of the crack, the process of crack propagation prevails over the process of plastic deformation in voew of the limited maneuverability of dislocations. We shall refer to temperature T_1 as transition temperature: below it, plastic deformation of monocrystals is subject to certain limitations, above it it progresses without kimitations. Such a division may appear to be overly acute, but the seemingly finely honed problem regarding the onset of the secondary creep system becomes manifested very acutely in polycrystalline materials where the same transition temperature T_1 will correspond to transition from incapability for plastic deformation at lower temperatures to capability for plastic deformation at higher temperatures.

Crystals always contain inclusions, specifically in the form of a solid solution or precipitates. Their effect on mechanical properties can become manifested in two ways: they either tie down old dislocations and in so doing reduce the density of mobile dislocations, or they act as obstacles to the mobility of mobile dislocations and in so doing reduce their median velocity.

Inclusions are of particular importance in NaCl type ceramics, because in view of low PN in the basic creep system, the extent of the creep limit is decided by the interaction of dislocations with inclusions. The greatest reinforcing effect is provided by cations of a different valency which cause great distortion in the adjacent parts of the lattice. The effect of nonstoichiometric composition of the crystal is also somplicated: at lower temperatures it leads usually to reinforcement, at higher temperatures to softening, probably due to easier diffusion [7].

5.2.2 Other Types of Ionic Crystals

ThO_2 and UO_2 also crystallize in a CaF_2 type lattice and ZrO_2 also has a similar lattice (only slightly deformed to monoclinic). Directions $\langle 110 \rangle$ of this cubic lattice [2] show great density of ions with identical charge and, thus, Burgers' vectors of mobile dislocations $b = \frac{1}{2} \langle 110 \rangle$ are similar to those of the NaCl type lattice; in comparison to this lattice, however, basic creep planes occur in CaF_2 crystals at lower temperatures of the plane $\{001\}$, secondary creep planes $\{111\}$ and $\{110\}$ occur only at higher temperatures. CsCl type crystals also have a simple lattice with easily mobile dislocations in the basic creep system only. The problems encountered in the case of these crystals with temperature are similar to those in NaCl type crystals [8, 9].

Other more complex ionic crystals differ in that their basic creep systems shows little mobility of dislocations. Due to their complexity there are no easy directions for creep making it possible to avoid ions of the same sign and dislocations are exposed to a high PN. It is most probably reinforced also by a considerable magnitude of Burgers' vector and, thus, high energy of dislocation.

A great amount of attention has been devoted to corundum (Al_2O_3); /10
complicated theoretical models [10] have been developed to describe

the properties of dislocations in its lattice. At lower temperatures the dislocations are practically immobile, mobility is basal planes was observed from 900°C on up, more significant plastic deformation above 1200°C. Mobility of dislocations in prismatic and pyramidal planes is possible only at higher temperatures, but even at 1700°C their mobility requires up to a tenfold stress than is the case in basal creep.

Among the more complicated ionic crystals most attention was devoted to examination of the mechanical properties of minerals occurring in the Earth's crust (see, e.g., the chapter on minerals in [11]). Let us use as an example spinel $MgAl_2O_4$ which has a cubic lattice and basic creep systems $\frac{1}{2}$ <110> $1\bar{1}1$, i.e., identical to metals with a k.pl.c lattice and, consequently, an adequate maneuverability of dislocations, to the extent that they are mobile. Nevertheless, due to high PN stress it is capable of attaining more significant plastic deformation only above 1700°C.

5.2.3 Covalent Crystals

Purely covalent substances such as diamond, Ge and Si crystallize in a diamond lattice which can be visualized as two intersecting cubic planarily centered lattices displaced by $\frac{1}{4}$ {111} . As the k.pl.c lattice can be represented as an arrangement of most densely covered planes of the {111} type in an *ABCABC*... sequence, a diamond lattice can be characterized by the planes sequence of $A\alpha B\beta C\gamma$... (see, e.g., [10]). Every atom is surrounded by four neighbors bonded by covalent directional bonds and the closest neighbors of each atom form the corners of a regular tetrahedron. The dislocations have identical Burgers' vectors $b = \frac{1}{2}$ <110> and identical creep planes {$1\bar{1}1$} same as k.pl.c metals. They thus possess good maneuverability, but lower mobility than metals. During mobility of dislocations there must occur alternate disruption and establishment of the directional covalent bond (Figure 3) and the PN barrier (per single-atom length of the dislocation line)

is equal to its energy. The corresponding PN stress can be estimated to several GPa (at a temperature of 0 K), approaching the order of ideal strength. Thus, mobility of dislocations can occur only with the aid of thermal activation; there again exist transient temperature (around 400° C for Ge and 600° C for Si), below /11
which the crystals are brittle, while at higher temperatures they are workable similarly to k.pl.c metals [12].

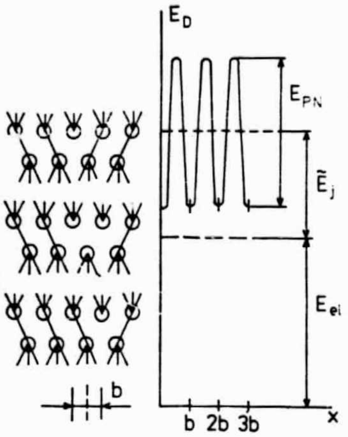

Figure 3. Mobility of Dislocation in a Diamond Lattice Calling for Alternate Interruption and Establishment of Directional Bonds and Corresponding to Fluctuation of Diclocation Energy E_D.

Thus, transition temperature here is of an entirely different origin than in ionic NaCl type crystals (where it is connected to changes in the maneuverability of dislocations), being caused by a change in the mobility of dislocations. We encountered this cause also in an ionic crystal with a complicated, but a highly symmetrical lattice, in spinel $MgAl_2O_4$. Even in this case transition temperature will be designated T_1.

Sphalerite lattice is an analogy of a diamond lattice with the difference that both k.pl.c lattices contain different types of atoms, e.g., in crystals of ZnS (low-temperature phase), GaAs, β-SiC, etc. The lattice remains cubic with alternation of planes {111} $A\alpha B\beta C\gamma$ and the properties of dislocations are analogous to those in a diamond lattice.

A wurtzite lattice, e.g., ZnS (high-temperature phase), AlN, α-SiC, corresponds to alternation of planes in an $A\alpha B\beta A\alpha B\beta$ sequence which makes it hexagonal and from the geometrical viewpoint, the properties of dislocations in it are similar to those in hexagonal metals with tight arrangement; of course, due to covalent bond their mobility is limited under transition temperature [2, 12].

In more complicated crystals (to include the wurtzite lattice) and, similarly, in more complex ionic crystals (to include Al_2O_3) the limited workability below transition temperature T_1 is participated by both phenomena, reduced mobility as well as maneuverability of dislocations.

5.3 Plastic Deformation of Polycrystalline Ceramics

5.3.1 Propagation of Creep Across Grain Boundaries

In plastic deformation of workable polycrystalline materials, the grain boundaries act at low and medium temperatures as obstacles to the mobility of dislocations. Sources of dislocations within grains emit dislocations which amass at the boundary and only after the front of the mass generates in the adjacent grain sufficient tension, a new creep band in the adjacent grain becomes linked to the end of the creep band (Figure 4a). The second possibility for relaxation of tension at the front of the creep band is occurrence of a crack along the grain boundary (Figure 4b) which can be expected to occur in materials with a reduced strength of grain boundaries.

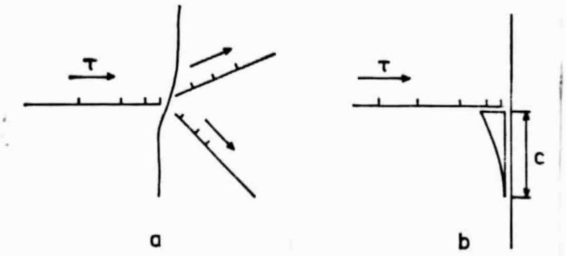

Figure 4. Accumulation of Dislocations Ahead of Grain Bounary Leading to: a) propagation of creep into a second grain; b) occurrence of cracks.

However, first let us have a brief look at the principial limitation of the workability of polycrystalline materials in cases where dislocations within grains do not possess sufficient maneuverability.

5.3.2 Number of Independent Creep Systems, von Mises' Criterion and Maneuverability of Dislocations /12

After plastic deformation of a polycrystalline material the lattice must have five independent creep system so that individual grains can acquire a random shape for mutual shape adjustment preventing occurrence of cracks between them for principial geometrical reasons.

This so-called von Mises' criterion (see, e.g., [13]) is based on the fact that one creep system can endow the crystal with a single very special mode of plastic deformation, pure shear. The creep system constituted by Burgers' vector $b^{(k)}$ and the unit normal of the creep plane $V^{(k)}$ thus yields elementary deformation $e_{ij}^{(k)} = \frac{1}{2}(b_i^{(k)} v_j^{(k)} + b_j^{(k)} v_i^{(k)})$. Hereby applies that $e_{11}^{(k)} + e_{22}^{(k)} + e_{33}^{(k)} = 0$, because no change in volume occurs through creep; thus the plastic deformation tensor has only five independent components. In the crystal there are N creep systems and, thus, N possible elementary deformations $e_{ij}^{(k)}$, $k = 1, 2, \ldots N$. If we want to combine a random deformation e_{ij}^{0}, which causes no change in volume, with the aid of elementary deformations from individual creep systems, we /13 seek for constants $C^{(k)}$ which would yield $\sum_{k=1}^{N} C^{(k)} e_{ij}^{(k)} = e_{ij}^{0}$. The precondition for solution of these equations is the requirement that the matrix of elementary deformations $e_{ij}^{(k)}$ have a rank of $H = 5$. This then is a mathematical representation of von Mises' criterion: a crystal must have five independent creep systems, i.e., five linearly independent elementary deformations.

Table 3 lists the creep systems and meeting of von Mises' criterion for selected crystals. For example, for NaCl type crystals

Table 3. Creep Systems of Selected Crystals

Typ mřížky (A)	Krystal (B)	Základní skluzový systém (C)				Vedlejší skluz. systémy nad teplotou T_1 (H)		Celkový počet nezávislých skluzových systémů nad T_1 (K)
		směr skluzu (D)	rovina skluzu (E)	počet skluz. systémů (F)	počet nezávislých skluz. systémů (G)	směr skluzu (I)	rovina skluzu (J)	
Rock salt	AgCl, NaCl LiF, MgO	$\langle 110\rangle$	$\{1\bar{1}0\}$	6	2	$\langle 110\rangle$	$\{001\}$	5
Fluoride	CaF_2, UO_2	$\langle 110\rangle$	$\{001\}$	6	3	$\langle 110\rangle$ $\langle 110\rangle$	$\{1\bar{1}0\}$ $\{1\bar{1}1\}$	5
Wurtzite	BeO, AlN	$\langle 11\bar{2}0\rangle$	(0001)	3	2	[0001]	$\{1\bar{1}00\}$	4
Corundum	Al_2O_3	$\langle 11\bar{2}0\rangle$	(0001)	3	2	$\langle 11\bar{2}0\rangle$ $\langle 10\bar{1}2\rangle$	$\{1\bar{1}00\}$ $\{\bar{1}011\}$	5
Hex.	C-grafit	$\langle 11\bar{2}0\rangle$	(0001)	3	2	–	–	2
Spinel	$MgAl_2O_4$	$\langle 110\rangle$	$\{1\bar{1}1\}$	12	5	–	–	5
Diamond Sphalerite	C, Ge, Si ZnS, β-SiC	$\langle 110\rangle$	$\{1\bar{1}1\}$	12	5	–	–	5
k.pl.c. metals	Al, Cu, Ni, γ-Fe	$\langle 110\rangle$	$\{1\bar{1}1\}$	12	5	–	–	5

Key: (A) Type of lattice; (B) Crystal; (C) Basic creep system; (D) Creep direction; (E) Creep plane; (F) Number of creep systems; (G) Number of independent creep systems; (H) Secondary creep systems above temperature T_1; (I) Creep direction; (J) Creep plane; (K) Total number of independent sheer systems above T_1.

with a total number of basic creep systems of $N = 6$ there exist two independent creep systems; thus, some types of deformation cannot take place. However, taking the basic and secondary creep systems together, then $N = 12$ and $H = 5$ and the von Mises' criterion is met. The von Mises' criterion for basic creep systems is not met in many ceramic materials and, thus, intercrystalline fracture can occur at lower temperatures sooner then the activity of secondary creep systems can be induced.

The workability of polycrystalline materials is attainable even when the von Mises' criterion is not met by the basic creep systems, provided that another process of plastic deformation is added. Such a process can be at high temperatures not only the onset of secondary creep systems, but also climbing of dislocations and diffusion creep. At low temperatures, when grain boundaries are sufficiently strong, stress can increase so that it will induce creep in creep systems not usually encountered before occurrence of cracks on the boundaries.

From the von Mises' criterion it follows that creep in individual grains will progress in keeping with several creep systems. However, this fact can lead to further limitation of workability, as it calls for potential mutual intersection of dislocations and of entire creep bands, which is not essentially required in monocrystals where even a large plastic deformation can be provided by a single creep system. However, in many ceramic substances this intersection of dislocations is difficult to achieve at lower temperatures, reactions between dislocations can also produce immobile dislocations and intersection of creep bands produces microcracks which increase with additional dislocations.

Thus,from the viewpoint of workability of polycrystalline materials, good maneuverability of dislocations can be characterized by two prerequisites: meeting of von Mises' criterion and the potential for easy intersection of dislocations.

5.3.3 Strength of Grain Boundaries

Even though the structure of grain boundaries at various types of bond is similar [14], boundary strength can undergo considerable changes due to the effects of bond. Metal bond shows relatively little dependence on precise arrangement of the closest neighbors and, thus, strength of grain boundaries (as long as they contain no impurities) is in metals close to the strength of the cores' interior.

Covalent bonds are directional and have a short range, so that any changes in the structure of the surroundings, in the number of the closest neighbors and distances between atoms lead to weakening of some bonds and a commensurate lower strength of grain boundaries. Even in ion crystals there can occur coming of ions of the same sign closer together along the boundary with a commensurate reduction in boundary strength.

Thus, in ceramic materials--in contrast to metals--grain /14 boundaries can considerably reduce strength. In pure materials without pores such strength reduction can reach 50% in comparison to the ideal strength of the grains' interior; yet the boundary strength would still remain high. In ceramic materials prepared by sintering the grain boundaries contain pores and some other various phases, particularly in the case of traditional ceramics. Therefore, in connection with limited mobility and maneuverability of dislocations within grains, in ceramics below transition temperature the boundaries are the weakest link and a place where brittle fracture can propagate at stresses that are not sufficient to induce plastic deformation within grains.

5.3.4 Macroscopic Plastic Deformation

A more conspicuous plastic deformation can be observed only above transition temperature which, however, is partially dependent on the type of stress exposure. Figure 5 shows tensile deformation curves of polycrystalline MgO at varying temperatures. At temperatures below 1700 C the sample sustain damage at about 30 MPa by brittle fractures, above 1700°C the samples become deformed by tens of percent the same as metals. Under exposure to uniaxial compression the transition temperature is lower; in sintered MgO it is possible to achieve permanent contraction on the order of several percent in a temperature range of 800 to 1200 °C in dependence on grain size and contents of pores.

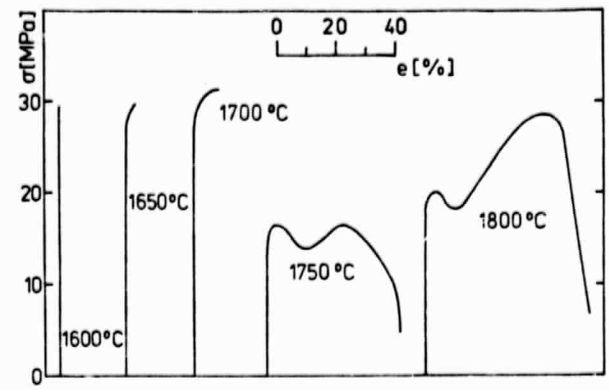

Figure 5. Curves of tensile strength σ - relative elongation e for polycrystalline MgO without pores at varying temperatures at deformation velocity of $\dot{e} = 5.10^{-4}s^{-1}$ (in accordance with [16]).

The most conspicuous reduction of transition temperature was achieved for the time being by combination of uniaxial tension with all-round stress exposure. This phenomenon is of importance to geology and, over the past several years, to the military sphere, because at the moment of the projectile's impact there occurs in the material ahead of the projectile a combined tension with a high component of hydrostatic pressure. The behavior of BeO, AlN and Al_2O_3 at high pressures was examined from this aspect in [15]. At superimposed uniaxial compression these materials in polycrystalline state are capable of plastic deformation of up to 10% even at room temperature, whereby they significantly absorb energy.

The greater ease of workability of ceramics under pressure, /15 particularly with a large component of hydrostatic pressure, is understandable: under these conditions the strength of grain boundaries is sufficient to induce at increasing shear stress mobility of dislocations and the activity of secondary creep systems within grains.

Except for model materials, particularly pure oxidic ceramics, the findings regarding plastic deformation in polycrystalline ceramics are very limited or still missing. This is due to the fact that transition temperatures are so high that plastic deformation in that region received little study, while below critical temperature damage by brittle fracture progresses without any significant plastic deformation.

5.4 Creep of Ceramics

Ceramic materials are often used at high temperatures, specifically at low tensions. Under these conditions the main limitation to their use in long-term exposure can be creep deformation or fracture during creep [16].

The progress and mechanisms of creep (i.e., time-dependent components of deformation) of ceramics are practically identical to those in metals and alloys. They can be divided into two groups: mechanisms progressing inside grains and mechanisms progressing on their boundaries.

In the first group deformation progresses primarily by creep of dislocations, however, its velocity is controlled by climb of dislocations or by carrying along of impurities. Significant among mechanisms of the second group are creep slippages along grain boundaries accompanied by occurrence and growth of cavities and, further, diffusion creep, during which lattice vacancies are diffused from one boundary point to another either through the grain's interior (Nabarro-Herring creep) or along boundaries (Coble's creep).

The theories of creep formulated originally for metals do not include some typical properties of ceramics such as porosity, occurrence of a second (often vitreous) phase along grain boundaries and the fact that it involves compounds with varying behavior of anions and cations [16]. Dimensions of grains are usually smaller in ceramics than in metals (sometimes up to 1 μm) and, consequently, diffusion mechanisms of creep are of greater significance to ceramics.

The peculiarity of creep in ceramics is the fact that in contrast to plastic deformation, creep deformation can progress even below transition temperature. Thermal activation facilitates slow creep mobility of dislocations with high PN stress, climbing of dislocations and diffusion mechanisms of creep replacing the inadequate maneuverability of creep mobility of dislocations. This, of course, involves slow deformation, nevertheless, e.g., fine-grained MgO becomes elongated at a temperature of 1200°C (i.e., way below transition temperature) even under the effects of small tensile stresses on the order of 1 MPa by 3% in 10 years [16].

5.5 Summary of Causes for Limited Workability of Ceramics

The conspicuous property of known ceramic substances in polycrystalline state is existence of transition temperature T_1 below which they are practically incapable of plastic deformation and above which they become workable. The reasons why plastic deformation cannot occur in polycrystalline ceramics below temperature T_1 can be divided into three groups:

A) Failure to meet von Mises' criterion and difficult intersection of dislocations, i.e., low maneuverability with simultaneous good mobility of dislocations (in this case the monocrystals are workable), e.g., in MgO.

B) Poor mobility of dislocations due to effects of a high PN stress with simultaneous good (potential) maneuverability of dislocations, e.g., in diamond, β-SiC and $MgAl_2O_4$.

C) Both of the preceding causes simultaneously, i.e., low mobility and maneuverability of dislocations. This group includes /16 most ceramics, e.g., Al_2O_3, SiO_2, α-SiC, Si_3N_4, etc.

Of course, the call for improved workability of ceramics in technical applications does not have as its objective attainment of high plastic deformation but, rather, formation of a plastic zone on the face of cracks to prevent brittle fracture. Thus, there is a need for orienting attention toward understanding the process of fracture, i.e., nucleation and propagation of cracks in ceramics and discovering processes that can inhibit fracture.

6. Occurrence and Propagation of Cracks

6.1 Measure of Brittleness

Fracture is a process of nucleation and propagation of cracks, whereby nucleation of cracks in ceramic substances is easy, or is no factor in view of the presence of a priori cracks, so that the key problem is crack propagation.

Brittle or strong behavior is then related to the resistance offered by the material against propagation of a sharp crack which can be quantitatively characterized by the effective nominal energy of rupture γ_{ef} ; i.e., the energy that must be expended on occurrence of a unit area of a crack.

The minimum energy required for generation of a unit area of a crack in compact material is $2\gamma_0$, where γ_0 is surface energy. The latter is understandably small, on the order of 1 J/m^2 at 0 K; it tends to slowly decrease with temperature. The key defense against crack propagation in crystalline materials is absorption of energy during mobility of dislocations in the plastic zone at the face of the crack, γ_{pl} , the major part of which undergoes transition into heat, the smaller part remaining stored in the area adjacent to the crack as energy of dislocations and other interference phenomena. Another part of the absorbed energy γ_{kin} is transformed into kinetic energy of elastic waves emitted from the face of the crack, eventually also into kinetic energy of fragments in the concluding stage of fracture. It is low at the onset of crack propagation. In general it applies that $\gamma_{ef} = 2\gamma_0 + \gamma_{pl} + \gamma_{kin}$.

The measure of brittleness or strength often used in fracture mechanics is fracture strength K_{IC} , i.e., critical value of the coefficient of stress intensity which is related to effective fracture energy by the relation $\gamma_{ef} = [(1 - \nu^2)/E]\, K_{IC}^2$ [16, 17].

The strength of metals is due to the fact that contribution of the plastic zone leads to $\gamma_{p1} \approx (10^4 \div 10^5)$ J/m^2 and exceeds the contribution of the surface stress by 4 to 5 orders. Thus, brittleness of some crystalline materials is the consequence of inadequate absorption of energy by mobility of dislocations under the conditions prevalent in the face of the crack.

Ceramic materials are sometimes divided into three groups according to their fracture behavior at room temperature [17]:

a) Completely brittle--incapable of plastic deformation at room temperature. These include ceramics with a high PN stress (Al_2O_3, SiO_2, TiC, SiC, Si_3N_4, etc.).

b) Brittle (also called semibrittle)--capable of at least a limited measure of plastic deformation at room temperature. They include ceramics with good mobility but poor maneuverability of dislocations (MgO, UO_2, ZrO_2 as well as NaCl, LiF, CaF_2).

c) Strong: this groups includes ionic crystals with transition temperature T_1 below room temperature, e.g., AgCl, CsCl, TlBr, etc., but, regrettably, no ceramic substances suitable for practical application.

It is obvious that this division can be expanded to the area /17 of higher temperatures. Materials of groups a), b) retain their brittleness or semibrittleness up to transition temperature T_1; above this temperature they are as strong as materials in group c).

6.2 Fracture in Monocrystals

6.2.1 Nucleation of Cracks

a) Completely brittle ceramics, even in the shape of monocrystals at tensile stresses on the order of $E/1000$ becomes subject to sudden damage by brittle fracture emanating from the surface. It is assumed that it contains a priori surface cracks on the order of 1 μm, the occurrence of which is not easy to prevent even with careful handling (they occur, e.g., through impact of grains of sand on the surface from a height of several centimeters, because local stress reaches theoretical strength).

b) Semibrittle crystals are almost equally sensitive to a priori surface cracks and brittle fracture propagates from these nuclei at tensile stresses. The cracks nucleate easily also as a consequence of mobility of dislocations concentrated into narrow creep bands, either near the surface or in points of band intersection. These causes of nucleation gradually disappear with increasing of temperature.

c) Strong crystals are not sensitive to a priori cracks and plastic deformation progresses without nucleation of sharp cracks.

6.2.2 Propagation of Cracks

a) In completely brittle crystals a crack of length propagates when tensile stress reaches the critical value of the so-called Griffith's stress $\sigma_{Gr} \approx \sqrt{(\gamma_{ef} E/c)}$ for $\gamma_{ef} \approx 2\gamma_0$. The mechanism of propagation is interference with atomic bonds at the face of the crack due to concentration of tension which locally reaches the value of ideal strength.

Even at lower tensile stresses, during long-term exposure there occurs a slow growth in subcritical cracks. After a certain time the crystal sustains damage which depends on the stress, chemical composition of the ambient medium and on temperature. The same effect is observed in glasses and is referred to as static fatigue or delayed fracture. This subcritical growth of cracks is caused, on the one hand, by chemical damage to the bonds at the face of the crack and, on the other hand, by contribution of thermal activation to damaging these bonds under tension. The velocity of crack propagation increases after reaching of critical magnitude sharply up to limiting velocity, approximately 0.4 of the speed of sound in materials.

Measurements for some crystals showed $\gamma_{ef} > 2\gamma_0$, e.g., for crystals of sapphire $\gamma_{ef} \approx 25\ \mathrm{J/m^2} \approx 20\gamma_0$. Thus, it appears probable that even in some completely brittle substances dislocations are emitted to short distances from the face of the crack under the effects of high concentration and absorption of energy is thereby increased. The γ_{ef} of sapphire continues to conspicuously increase above 900 °C and the face of cracks starts showing formation of a plastic zone [17].

b) Subcritical cracks in semibrittle crystals grow first under the effects of of the progressing small plastic deformation, e.g., by introducing edge dislocations from the creep band into the crack. However, after attaining critical magnitude the crack propagates /18
similarly as in completely brittle materials with γ_{ef} on the order of $2\gamma_0$ (e.g., for MgO monocrystals at room temperature it is $\gamma_{ef} \approx \approx 1.3\ \mathrm{J/m^2}$). Thus, mobility of dislocations by itself is not sufficient, formation of an effective plastic zone calls for good maneuverability as well.

c) Ceramic crystals show strong behavior only above transition temperature. The fracture then progresses as workable. For example, cracks do not occur and propagate at temperatures in excess of 1600°C at suitable orientation of a MgO crystal which then is sheared along plane (110) to zero diameter.

6.3 Fracture in Polycrystalline Ceramics

Polycrystalline materials prepared by sintering show a number of effects that promote occyrence of fracture along grain boundaries:

1. Presence of pores, particularly on grain boundaries.

2. A priori cracks for easily along grain boubdaries and to a greater depth than in monocrystals and they practically defy elimination.

3. Microcracks occur along grain boundaries as well as under the effects of internal thermal stresses.

4. Grain boundary represents a weak point due to the effects of inadequate linkage of covalent and ionic bonds, particularly in the presence of impurities and other phases along the boundaries (γ_{ef} can be smaller than $2\gamma_0$).

5. Failure to meet the von Mises' criterion causes occurrence of cracks along grain boundaries already during small plastic deformation caused by mobile dislocations within grains.

a) Completely brittle ceramics at low and medium temperatures and at increasing tensile stresses becomes suddenly subject to damage by brittle fracture with an intercrystalline progression and originating from an a priori surface crack. Various empirical relations have been proposed for bending strength R_0 in relation to porosity P and medium grain size d, e.g., Knudsen's relation 16 $R_0 = S_x d^{-a} e^{-bP}$, where S_x, a, b are experimentally determined parameters; the value of ranges between $\frac{1}{3} < a < 1$. Greatest strength in ceramics can be attained at low porosity, small grain dimensions and an optimally smooth surface where even dimensions of a priori cracks remain very small.

b) Even in semibrittle materials a crack propagates as brittle below transition temperature and originates usually from an a priori surface crack, but shows not just intercrystalline propagation. During intersection of creep bands in individual grains there namely occur and propagate cracks also within grains. Bending strength can again be expressed--depending on porosity and grain size--by Knudsen's relation.

c) Two thermal regions must be considered at high temperatures and sufficiently high tensions when creep alone is not enough.

Below transition temperature T_1 there already occur creep-like slippages along grain boundaries, however, low mobility and maneuverability of dislocations still are inadequate for adapting the shape of grains. Thus, these slippages form a great many cracks along grain boundaries and become gradually interconnected; in the final stage there occurs sudden fracture in the remaining part of the section.

Above transition temperature polycrystalline ceramics without pores behaves as strong and sustains damage through plastic fracture, because plastic deformation within grains is enough for accommodating the shape of grains during creep slippages. On the other /19 hand, ceramics with pores does not attain great strength, because expansion of pores into cracks cannot be effectively prevented during creep slippages along grain boundaries [16].

Fracture in creep of ceramics under exposure to low stress shows considerable difference from high-temperature fracture of ceramics under exposure to high stress. Transition temperature is not of decisive significance, because even below this temperature the sample is capable of slow deformation on the order of up to several percent by means of creep mechanisms. The typical fracture process in creep of ceramics is gradual expansion of pores, new cavities and their interconnection due to creep slippages along grain boundaries and diffusion ending by a sudden fracture [18].

6.4 Concluding Remarks on the Brittleness of Ceramics

The main reason for easy propagation of cracks in ceramics below transition temperature is the fact that a plastic zone cannot develop at the face of the crack due to low mobility and maneuverability of dislocations and the values of γ_{ef} (in monocrystals and in monocrystalline materials) are by 4 to 5 orders lower than in metals.

Another important reason is the presence of a priori surface cracks, so that the nucleation stage, as a rule, does not materialize in ceramics. The intercrystalline character of fracture is supported by imperfect connection of grain boundaries, by the presence of pores on grain boundaries and internal heat tensions.

Ceramics' easy sustaining of damage during exposure to impact stress is connected to the fact that high tensions are generated at the moment of impact; in view of insufficient plastic deformation and internal attenuation throught the sample's entire volume the prevalent part of impact energy is first converted into elastic energy.

7. Potential for Improving the Mechanical Properties of Ceramics

7.1 Strength Improvement

Griffith's criterion (para 6.2.2) offers two basic approaches to improvement of strength, either reducing the length of cracks (or their elimination), or increasing of γ_{ef}, i.e., increasing the resistance against crack propagation. Another approach is increasing of the elasticity modulus which can become manifested in ceramics as a small side effect in reducing of porosity.

Great strength of ceramics can essentially be achieved by elimination of cracks, however, in view of the easy nucleation of cracks in ceramics, this procedure does not appear to be a technically viable solution.

A basic improvement of the mechanical properties of ceramics could thus be achieved only through improving its strength, either by reducing the transition temperature or by at least a modest improvement of its toughbess below transition temperature.

The approaches used up to now in achieving a modest increase in the strength of new ceramics (improved sintering process leading to lower porosity and improved grain linkage, selection of ceramics with low expansibility and high thermal conductivity) led to increasing the values of from 1 J/m on the order of 100 J/m at which, however, the material still remains brittle. The reason is that an effective plastic zone cannot be developed in new ceramics, /20 because the key causes of brittleness had not been eliminated.

We are of the opinion that in long-term outlook there is a need for examining the possibility for achieving a conspicuous increase in the strength of at least some types of ceramics by forced occurrence of a plastic zone at the face of cracks. After all, limited mobility and maneuverability of dislocations are not absolute properties; dislocations can move under exposure to high stress and secondary creep systems can be forced to occur even below transition temperature; moreover, critical temperature can be controlled. However, approaches to increasing the strength of ceramics by improving its workability are still at the stage of tentative search.

We are listing several measures which could lead to acieving another conspicuous improvements in strength through the following approach:

1. Another significant increase in the strength of grain boundaries. This measure should lead to forcing a greater mobility of dislocations with a higher PN stress and forcing the functioning of secondary creep systems. To assess the potential offered by this approach we must expand our knowledge of the structure and properties of grain boundaries in substances with ionic and covalent bond and the role of impurities on grain boundaries.

2. Improving the maneuverability of dislocations by admixtures. Literature on ceramics mentions from time to time that admixtures and deviations from stoichiometry variously affect the thermal

dependence of creep tension for basic and secondary creep systems, however, systematic measurements are still missing.

3. Increasing the density of mobile dislocations. Dislocations in substances with a low PN tension are often immobile, because they are anchored by admixtures in the course of the preceding thermal processing. An increase in the density of mobile dislocations can be achieved either by improved purity, or by processes which introduce fresh dislocations post facto (surface finishing, effects of high pressures, etc.).

4. Utilization of pressure tensions. Transition temperature is lower at compression stresses, which offers a solution in having the components operate with prestressed compression or at least with internal compression tensions near the surface (similarly as in glasses).

5. Systematic development of multiphase ceramic materials. While traditional ceramics is multiphase, the selection and connection of phases is utterly unsuitable from the viewpoint of strength. New ceramics has been introduced up to now rather in single-phase form, admixtures or additional phases being used for improving the sintering process. Systematic development of multiphase systems is in ceramics--from the viewpoint of improvement of mechanical properties--at the very beginning. Nevertheless, there is already isolated use of the term "ceramic alloys."

Development of new types of ceramics with improved mobility and maneuverability remains an unresolved problem of basic research and neither the current practice nor specific projects cannot rely on its early solution.

As very promising is regarded increasing of strength by other processes which would be capable of absorbing energy in the sphere of concentration of tensile stresses at the face of cracks and relax these stresses, i.e., create a substitute for the plastic zone by a suitable "process" or "relaxation" zone. Such a process would make it possible to force phase transformations by stress and, surprisingly also occurrence of a large number of microcracks, inasfar as they cannot contribute to propagation of the main crack. Holding promise in this respect is ZrO_2, in which phase transformation occurs between 900 to 700°C, during which the volume of the low-temperature phase in higher by approximately 3% [19]. This phenomenon is used in two ways. In the first way, around small particles of ZrO_2 (after cooling and completion of transformation) in the surrounding matrix (e.g., Al_2O_3, Si_3N_4) there occur great tensile stresses which lead to occurrence of microcracks. The latter open up slightly in the process zone at the face of the crack, thus reducing the concentration of stress and energy is absorbed. The /21 second way uses various admixtures to stabilize the high-temperature phase of ZrO_2, then phase transformation of ZrO_2 particles progresses in the process zone due to the effects of tensile stresses, whereby the transformed particles increase the volume and decrease the concentration of stresses in the matrix. In these two ways it became possible to increase the value of γ_{ef} in ceramics based on Al_2O_3 or on Si_3N_4 with an admixture of approximately 15% ZrO_2 from the previous top value of 100 J/m^2 to 500 J/m^2 [20].

In our opinion, generation of a process zone by use of phase transformations launches a new significant trend in the development of ceramics with increased strength. Good prerequisites are created for it by the richness of phase transformations in ceramics [3].

7.2 Ceramics in Composite Materials

One of the possibilities for using brittle ceramics in parts exposed to stress is its combination with other strong materials in composite substances. Use is made of two essentially varying methods:

1. Ceramic fibers of high strength improve the strength of a tough matrix, be it metal or polymer. In this case the brittleness of ceramic fibers poses no disadvantage and composites of this type currently belong among top materials with a high degree of toughness and strength. This, of course, involves materials that are essentially metals or polymers, even though the share of their ceramic component is up to 50 volumetric percent.

2. Metal, polymer or ceramic fibers are embedded into a ceramic brittle matrix to endow the composite with higher strength. In using metal fibers as filler (taking up 10% of volume) it became possible to increase the γ_{ef} of ceramics (e.g., Al_2O_3, MgO) up to 10^4 J/m^2, i.e., a value on the order approximating that of metals. Intensive research is progressing in the meantime in this area on a laboratory scale, the main difficulties being caused by internal stress due to varying thermal expansivity of the matrix and of fibers and, of course, deterioration in chemical and heat resistant properties [21].

Let us also call attention to the so-called cermets, e.g., sintered carbides [22] in which the hard component is formed by carbides (e.g., WC, TiC--i.e., ceramics) and the connecting component by metal (e.g., Co, Ta, Nb). These materials are outstanding for cutting tools, however, under the effect of tensile stresses the negative properties of both phases tend to come to the fore: low creep limit of the connecting material and brittleness of carbides. As carbide particles are not elongated, they cannot be adequately exposed to tensile stress and the material cannot compete with composites containing ceramic fibers. Yet, the strength of sintered carbides is better than that of traditional and new ceramics and attains values of γ_{ef} up to 1000 J/m^2.

Lastly let us call attention to "macroscopic composites", i.e., combinations of ceramics with metal, when the ceramic (brittle) layer on a metallic part is to provide protection against chemicals or heat, eventually provide resistance against wear, while the metallic component provides strength and toughness of the whole composite. This solution, routinely used in, e.g., rocketry, is finding applications in other areas of engineering.

8. Contemporary Technical Approach to Brittleness of Ceramics

Application of ceramics in engineering has been motivated primarily by its high melting point, chamical resistance, resistance to heat as well as its thermal and electric insulation properties. From among its mechanical properties, use was made of its good resistance against wear through sliding friction and, occasionally, of its good compression strength. Care was taken at the same time not to expose ceramic components to tensile and, particularly, mechanical and thermal impacts.

For that reason ceramic materials did not and do not belong /22 among material routinely used in construction of parts subject to stress exposures. This place is reserved for metallic materials, to which polymers were added to a limited extent for use at lower temperatures and some of their composites. Due to their high strength combined with toughness and thus also operational safety they make it possible to solve even the most demanding technical tasks at low and medium temperatures. However, as we pointed out in the introduction, their properties deteriorate under temperatures in excess of 1000°C to the point that technicians turn their attention to ceramics.

Nevertheless, use of ceramics in parts subjected to stress is at the present time a pioneering task, because it must come to terms with the brittleness of ceramics and with gradual propagation of cracks during operation.

Modern interdisciplinary approach constitutes the basis of the contemporary technical approach--fracture mechanics (see, e.g., sub [17, 23, 24]), which combines in prediction of fracture occurrence theoretical phenomenological description and experimental study of crack propagation. In considerations regarding the probability of sustaining of damage 16 use is also made of a statistical approach to the strength of brittle materials. This includes also conducting of safety tests, i.e., short-term overloading of parts that leads to fracture and, consequently, elimination of parts that would probably sustain damage prior to reaching their desired service life. Despite these measures and many structural measures a hundred percent safety of ceramic parts exposed to stress cannot be guaranteed. Thus, consequences of a potential breakdown must be taken into consideration.

Among the most closely detailed studies regarding the development of materials are those for internal combustion turbines, where the use of ceramics for many parts, to include turbine blades, is to allow increasing the input temperature up to 1400 C. Some 250 various ceramic materials received consideration, but only two of them, Si N and SiC,proved worth of firther experimentation 25 . Table 4 and Figure 6 show the properties of these materials under different methods of their preparation. Their selection was influenced mainly by their favorable thermal properties: SiC has excellent thermal conductivity, Si N has low thermal expansivity. While equally good in bending strength, from the viewpoint of behavior in thermal impacts these materials are superior to other ceramics. In view of their covalent bond and a complex lattice their PN stress is of course so high that even at 1400 C dislocations are practically immobile and permanent deformation at these temperatures can progress only through mechanisms of diffusion creep and sliding creeps along grain boundaries.

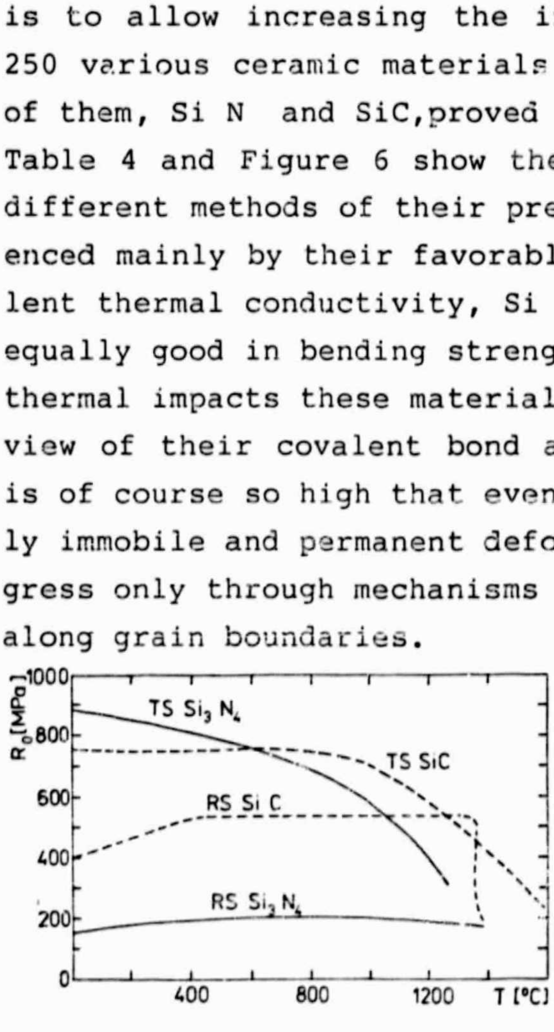

Figure 6. Dependence of bending strength R_0 on temperature for pressure-sintered (TS) and reaction-sintered (RS) Si_3N_4 and SiC (according to [25]).

Table 4. Properties of Materials Based on SiC and Si_3N_4 (average values between 0°C and 500 C, according to [25])
RS - reaction-sintered, TS - pressure-sintered

(1) Materiál	Objemová (2) hmotnost ϱ_v [kg/m^3]	Modul pruž. (3) v tahu E [GPa]	Pevnost (4) v ohybu R_G [MPa]	Tepelná (5) vodivost λ [Wm^{-1} deg^{-1}]	Tepelná (6) roztažnost α [10^{-6} deg^{-1}]	$R_1 = \frac{R_0}{E\alpha}$ [deg]	$R_2 = \frac{\lambda R_0}{E\alpha}$ [Wm^{-1}]	ef. lom. (7) energie γ_{ef} [J/m^2]
RS SiC	3 120	410	480	83	4,4	260	22 . 10^3	20
TS SiC	3 210	380	700	100	4,3	430	43 . 10^3	80
RS Si_3N_4	2 600	220	200	25	2,7	340	8,5 . 10^3	5
TS Si_3N_4	3 190	310	800	30	3,2	810	24 . 10^3	120

Key:
(1) Material
(2) Volumetric weight
(3) Modulus of Elasticity in Tension
(4) Bending Strength
(5) Thermal Conductivity
(6) Thermal expansivity
(7) Effective Fracture Energy

/23

Technical projects are concentrating on development of stationary high-output internal combustion turbines and development of turbines for trucks and passenger cars; these materials do not offer adequate safety for use in aviation. Practical applications for these turbines were envisioned for the years following 1985 [25], however, in view of the necessity for continued basic research [26] it appears probable that their introduction will be postponed to a more distant future. /22

9. Conclusion /24

Key causes of the brittleness of ceramics have already been clarified from their physical aspects. They consist in the fact that ceramics, in the state in which it is currently available, possesses insufficient defenses against propagation of sharp cracks below critical temperature. A plastic zone fails to form at the face of cracks due to low mobility and maneuverability of dislocations and low strength of grain boundaries.

Significant improvement of the strength of ceramics constitutes an unresolved problem in basic physical research. Approaches to induced formation of a plastic zone are currently being sought. Attempts to generate substitute process zones by inducing phase transformations at the face of cracks are very promissing, but are only in their initial stage of development. It is even possible that these approaches will not lead to complete success. Use of ceramics in composites brings about new types of materials with excellent mechanical properties, however, at the expense of sustaining losses in resistance to chemicals and heat.

Modest improvements in the mechanical properties of ceramics are achieved in technical field work by gradual technological improvements, particularly of the sintering process. However, this eliminates only the secondary causes of brittleness. Nevertheless, with the currently attained top values, technical field work still could find applications even for the persistently brittle ceramics, specifically in parts exposed to high temperatures, by means of a set of comprehensive measures. However, contemporary technology is not succeeding in producing ceramics with a reproducibility of properties which it routinely achieves with metals. Thus, the current technical problem is increased reproducibility of the properties of ceramics to warrant safety of operations. It is interesting to note that over the past several years technology is coming to the conclusion [26] that improved reproducibility of properties calls for a new wave of basic research in physicochemical processes in all phases of ceramic technology and of the microphysical processes occurring during its deformation.

Thus, the tasks faced by basic and applied research in mechanical properties of ceramics are extensive and difficult, yet, from the physical aspect, interesting and, at the same time, of extraordinary technical significance. Development of new materials for power engineering, increased operational temperatures, improved efficiency of heat generating machinery and heat engines as well as improvements in combustion should contribute to dealing with significant problems of the future--savings of energy and improvement of the environment.

For that reason, research of ceramic materials in advanced countries has been showing a considerable increase over the past ten years while also changing its orientation. What is typical of the new wave of research is the fact that to a considerable degree it is returning to basic research, that it is availing itself of all the experimental and theoretical methods originally developed for research in metallic materials and that the field of ceramic research is being entered by many researchers and research facilities engaged in research of metallic materials.

The possibilities for expanded application of ceramic materials in mechanical engineering are attractive from the CSSR viewpoint because the country has in this respect an adequate base of raw materials as well as a sound tradition in various areas of ceramic production and research. Help offered in expansion of research of the mechanical properties of ceramics by physical and technical facilities dealing with metallic materials would be most welcome.

REFERENCES

1. Kroupa, F., "Current State of Knowledge of the Physical and, Particularly, Mechanical Properties of Ceramic Materials and Their Potential Applications in Mechanical Engineering of the CSSR." Research Report Z-81-4537, State Research Institute for Materials, Prague 1981.

2. Kingery, W. D., Bowen, H. K. and D. R. Uhlmann, "Introduction to Ceramics." J. Wiley, New York 1976.

3. Levin, E. M. and H. E. Mc Murdie, "Phase Diagrams for Ceramists." American Ceramic Society, Columbus 1964, 1969, 1975, 1979.

4. Nye, J. F., "Physical Properties of Crystals." Clarendon Press, Oxford 1957.

5. Kelly, A., "Strong Solids." Clarendon Press, Oxford 1966.

6. Gilman, J. J., in: "Physics and Chemistry of Ceramics." (Klingsberg S., editor) Gordon and Breach, New York 1963, p. 240.

7. Mitchell, T. E. and A. H. Heuer, Mater. Science and Eng. 28 (1977), p. 81.

8. Sprackling M. T., "The Plastic Deformation of Simple Ionic Crystals." Academic Press, New York 1976.

9. Pask, J. A. and S. M. Copley, in: "Modern Ceramics." (Editors Hove, J. E. and W. C. Riley) J. Wiley, New York 1965, p. 86.

10. Amelinckx, S., in: "Dislocations in Solids." Nabarro, F. R. N. editor) North-Holland, Amsterdam, 1979, p. 67.

11. "Dislocations et deformation plastique" [Dislocations and Plastic Deformation]. (Groh, P., Kubin, L. P. and J. L. Martin editors) Yravals 1979.

12. Alexander H. and P. Haasen, Solid State Physics 22 (1968), p. 27.

13. Paterson, M. S., in: "Physics of Strength and Plasticity." (Argon, A. S., editor) MIT Press, Cambridge 1969.

14. Gleiter, H. and B. Chalmers, Progr. in Mater. Sci. 16 (1972),1.

15. Heard, H. C. and C. F. Cline, J. Mater. Sci. 15 (1980), p. 1889.

16. Evans, A. G. and T. G. Langdon, Progr. in Mater. Sci. 21 (1976), p. 171.

17. "Fracture," part 1 through 7. (Liebowitz, H., editor) Academic Press, New York 1968-1972.

18. Evans, A. G. and A. Rana, Acta Met. 28 (1980), p. 129.

19. Petzow, G. and N. Claussen, Radex-Rundschau 1977, p. 110.

20. Pratt, P. L., Metal Science 14 (1980), p. 363.

21. Donald, I. W. and P. W. McMillan, J. Mater. Sci. 11 (1976), p. 949.

22. Exner, H. E., Internat. Metals Reviews 24 (1979) p. 149.

23. "Fracture Mechanics of Ceramics," part 1 through 4 (Bradt, R. C., Hasselman D., P. and F. E. Lange, editors). Plenum Press, New York 1974-1978.

24. Kroupa, F., Cs. cas. fyz. A28 (1978), p. 101.

25. Lines, D. J., in: "High Temperature Materials in Gas Turbines." (Sahm, P. R. and M. O. Speidel, editors) Elsevier, Amsterdam 1974, p. 155.

26. Bowen, H. K., Mater. Science and Eng. 44 (1980), p. 1.

Submitted on 5 June 1981.