Review Paper

USE OF ZrO_2 PHASE TRANSFORMATION IN INCREASING FRACTURE TOUGHNESS OF CERAMICS

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INTRODUCTION

The problem of increasing the resistance of technical ceramics to brittle fracture is one of the issues which have been paid great attention to in recent years. This is a demanding project which includes a number of problems of the nature of basic research, such as the study of the mechanisms of transformation toughening, their mathematical description, application of the linear fracture mechanics theory to ceramic materials, composition and study of phase diagrams of new or little known systems, and the like. Applied research is concerned with technological problems, for example preparation of transformation-toughened materials of various chemical compositions, new procedures for preparing the initial raw materials (the sol-gel method, precipitation and co-precipitation), application of new technological processes in the field of heat treatment (hot isostatic pressing - HIP), grinding and polishing of sintered materials, preparation of fracture toughness specimens, etc.

In the field of assessing the properties of the final materials, attention is focused on fracture toughness testing, establishment of the temperature dependence of mechanical properties and of fracture toughness, application of electron microscopy and special X-ray analysis methods in the evaluation of structures and phase composition of the materials prepared.

From the standpoint of the existing ceramic practice, all these are new, untraditional approaches, on the satisfactory mastering of which depend the prospects of further development in the field of advanced ceramics. The results achieved during a relatively short time seem to justify the assumption that the brittleness of some ceramic materials, which has so far restricted their wider utilization as structural materials in technological practice, will actually be suppressed.

BRITTLE FRACTURE AND ITS ASPECTS WITH RESPECT TO CERAMICS

In consequence of their chemical substance, ceramic materials are held together by interatomic bonds of ionic and covalent character.

It holds in general that materials with ionic and covalent bonds exhibit a low resistance to brittle fracture.

This is the case because the degree of resistance to brittle fracture of a material is given by its ability to relieve concentrated outer or internal stresss by plastic deformation. The basic requirement for creating conditions for plastic deformation in a material exposed to mechanical stressing is a satisfactory mobility and maneuverability of dislocations in the crystalline lattice [1]. However, the character of bonds typical for ceramics, i.e. ionic and covalent ones, restricts significantly the mobility as well as maneuverability of lattice defects, thus suppressing to a minimum the tendency of material to plastic deformation.

A detailed analysis of the mechanism of plastic deformation shows that the low resistance of ceramics to brittle fracture is contributed to by additional factors such as a high inhomogeneity of their structure, concentrated in particular at grain boundaries, inter- and intracrystalline porosity, the presence of cracks and other macroscopic defects in the material, existence of internal stresses and some other effects [1]. The grain boundaries act as obstacles to movement of dislocations, their strength is low as a result of the presence of pores, various other phases, and the consequent imperfect joining of the individual grains. This is why the intercrystalline boundaries are the weakest link of the structure and the points where brittle fracture propagates at stresses which are not yet adequate for bringing about plastic deformation inside the grains.

The following two basic conditions have to be met to ensure a good maneuverability of dislocations:

1) von Mises'es criterion
2) ensuring the possibility of ready permeation of dislocations.

Von Mises'es criterion requires the existence of five independent glide systems in the crystalline lattice to ensure plasticity of a polycrystalline material. The gliding of dislocations in the individual crystals then takes place along several glide systems. At the same time, the dislocations and the complete glide bands should have the ability to permeate, which is quite dif-

Table I

A survey of special terms and their abbreviations used in the field of transformation toughening of ceramics

Item	Term	Abbreviation	Significance
1.	Transformation toughened ceramics	TTC	
2.	Zirconia-toughened ceramics	ZTC	ceramics toughened by t-m ZrO_2 phase transformation
	Zirconia toughened alumina	ZTA	Al_2O_3-ZrO_2 ceramics with ZrO_2 dispersed in Al_2O_3 matrix
3.	Tetragonal zirconia polycrystal	TZP	polycrystalline tetragonal ZrO_2
4.	Zirconia	ZrO_2	zirconium dioxide
	– cubic	c–ZrO_2	
	– tetragonal	t-ZrO_2	
	– monoclinic	m-ZrO_2	
	– orthorhombic	o-ZrO_2	
5.	Partially stabilized zirconia	PSZ	
	– magnesia PSZ	Mg-PSZ	stabilized with magnesium dioxide
	– calcia	Ca-PSZ	with calcium dioxide
	– yttria	Y-PSZ	with yttrium oxide
	– ceria	Ce-PSZ	with cerium dioxide
6.	Fully stabilized zirconia	FSZ	

ficult to ensure with polycrystalline materials, especially at low temperatures. Interactions between the dislocations also produce immobile dislocations, while intersecting of glide bands may cause microcracks to form.

These circumstances and the fact that most ceramic materials do not meet von Mieses'es criterion are responsible for the impossibility of ensuring adequate maneuvaribility of dislocations in polycrystalline materials. Jointly with the limited mobility of dislocations one can thus get the basic idea why ceramics are brittle, or why they are unable to relax local mechanical stresses by the plastic deformation mechanism.

The rules of crack propagation in materials, the description and prediction of the behaviour of materials subject to mechanical loading are all issues dealt with by fracture mechanics [2]. The so-called linear fracture mechanics, which is most suitable for ceremic and glassy materials, is based on the assumption that up to the moment of catastrophic fracture, the material is controlled by Hooke's law and that any possible plastic deformation will occur only in the closest neighbourhood of the crack root [3, 4, 5].

To describe quantitatively the degree of brittleness, fracture mechanics has introduced a new material constant, fracture toughness, K_{IC}. This is the critical value of the stress intensity factor, on attainment of which a critical crack growth and eventually fracture occurs.

The stress intensity factor is expressed in the form

$$K_I = \sigma \sqrt{a}\, Y,$$

where σ is the nominal tensile stress at the given point in a crack-free body,
a is length or some other characteristic dimension of the crack,
Y is a calibration factor which is a function of the dimensions of the body and the crack.

Linear fracture mechanics postulates the following relationship as a criterion of the crack stability, and thus also of the resistance of the material to brittle fracture:

$$K_I < K_{IC}.$$

TRANSFORMATION TOUGHENING OF CERAMICS UTILIZING THE POLYMORPHY OF ZIRCONIA

At present, it may be regarded as fully proved that the toughness of some ceramics can be significantly increased by means of zirconia in its tetragonal modification, dispersed or precipitated in the ceramic matrix [6-10]. The process is called transformation toughening.

In the course of time, a specific terminology and abbreviations have come into use in this field. They will also be employed in the present paper, and are summarized in Table I.

Transformation toughening proceeds in principle by two basic mechanisms [11, 12]:

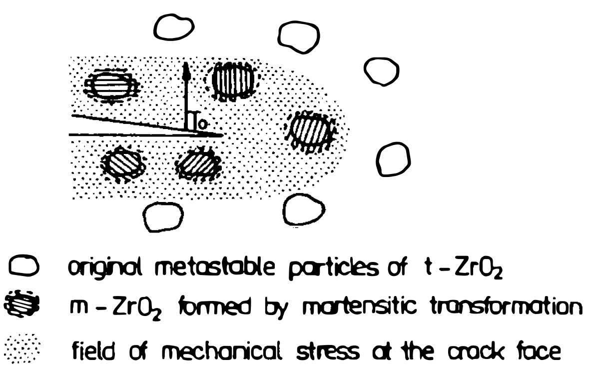

Fig. 1. Transformation of metastable t-ZrO_2 in the process zone of a propagating crack [11].

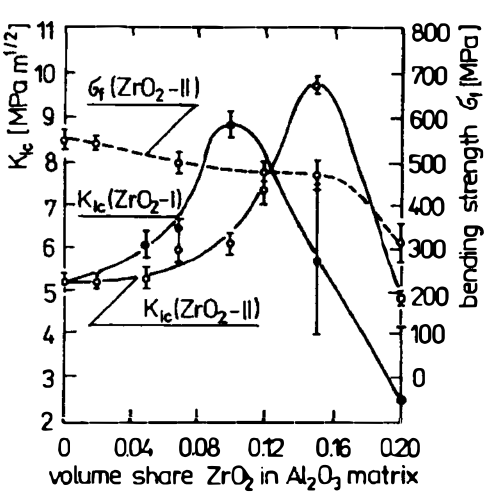

Fig. 3. Mechanical strength and fracture toughness of ZTA ceramics vs. ZrO_2 content in the material by volume [7]. ZrO_2-I initial raw material with 0.3 μm mean grain size, ZrO_2-II initial raw material with 1.3 μm mean grain size.

(1) By stress-induced transformation in the process zone of the crack propagating through the material (martensitic type of transformation),

(2) By nucleation of microcracks in the ceramic matrix.

Fig. 1 shows schematically the situation in a material with a propagating crack, where transformation toughening is effected by the mechanism of stress-induced transformation. In the neighbourhood, particularly at the crack face, great tensile stresses are generated and relieve the compressive effects of the matrix on the metastable particles of t-ZrO_2, transforming them to m-ZrO_2.

This process involves a change in volume by at least 3% and creation of substantial forces which generate compressive stresses in the matrix. These in turn form an energy barrier against further crack propagation. The mechanism raises both toughness and strength of the material.

The nucleation of microcracks in the matrix, as another mechanism suppressing the brittleness of ceramic materials, is implemented as a result of changes in volume in the t-ZrO_2 process during the cooling down below the transformation temperature of the system containing ZrO_2 particles. Tangential stresses are generated in the proximity of an m-ZrO_2 particle, formed by the t-m transformation process, and lead to microcracking in the matrix. The energy of the propagating crack is absorbed or dissipated at these defective points.

Fig. 2 shows the structure of a ZPA material with nucleated microcracks. The optimum state is attained when the ZrO_2 particles are adequately large to allow for spontaneous transformation, and at the same time adequately small so as to form a limited number of cracks and avoid occurence of catastrophic fracture. To ensure a satisfactorily high fracture toughness of the material, the dependence of the amount of ZrO_2 by volume dispersed in the matrix on the respective mechanical characteristics exhibits a very sharp peak, as indicated by the courses of the curves in Fig. 3.

In addition to the mechanisms described, also some others may take part, e.g. a combination of the two types mentioned above in sequence 1,2 or deviation or blunting of the crack during the t-ZrO_2 transformation.

The possibility of creating the so-called compression layer in ZTC materials is one of the significant aspects of the toughening of ceramics by utilizing the reversible transformation of zirconia. This is a surface layer of the material up to several tens of micrometers in thickness, in which spontaneous t-m transformation of ZrO_2 takes place and consequantly compressive stresses arise as a result of the absence of the force effects of the matrix. The state of compressive stress raises considerably the strength of the material. Grinding of the material surface, by which the metastable grains of tetragonal ZrO_2 in the surface are transformed to monoclinic ZrO_2, is one of the effective ways of preparing the compressive layer. The process is schematically illustrated in Fig. 4.

At first, the possibility of transformation toughening had only been considered with partially stabilized ZrO_2, where it was also discovered [6]. However, it was soon found that the process can also be applied to other ceramic materials, such as alumina, Si_3N_4, mullite and cordierite [7, 13–18].

POLYMORPHY OF ZIRCONIA

From the standpoint of physical chemistry, zirconia is interesting in that it is polymorphic in nature and in dependence on temperature and pressure exists in

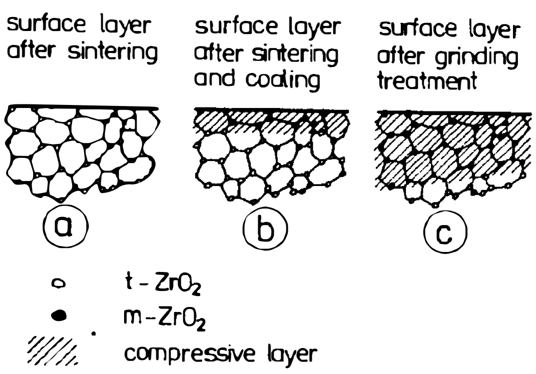

Fig. 4. Schematic illustration of the formation of a compression layer in ZTC materials [11].

several crystallographic modifications which are reversibly transformed one into the other at defined conditions [19–23], as shown by Table II.

Table II

Polymorphy of zirconia at atmospherical pressure

Melt	- fluorite structure
	- spatial group F_{m3m}
	- density 6.090 g cm^{-3}/20°C (calculated)
	- distorted fluorite structure
	- spatial group $P4_{2/nmc}$
	- density 6.100 g cm^{-3}/20°C (calculated)
	- distorted fluorite structure
	- spatial group $P2_{1/c}$
	- density 5.560 g cm^{-3}/20°C

The t-m ZrO_2 phase transformation, which in recent years has been studied extensively in connection with transformation toughening, exhibits the following charateristic features [19, 24]:

- shows a temperature hysteresis of about 200°C,
- is not associated with diffusion
- is martensitic in nature.

With the use of additions of some oxides, particularly those of alkaline and rare earths, it is possible, in dependence on the amount and type of the admixture, to attain a complete or partial stabilization of the high-temperature modifications of ZrO_2.

This measure expands the existence region of the cubic and tetragonal modifications, in some cases down to the room temperature region. For the purpose of transformation toughening, it is particularly important to preserve in this way the tetragonal ZrO_2 in the material. Under certain circumstances, its content may be up to 100% (the category of TZP materials).

Recently, some reports on the synthesis and properties of an additional crystallographic modification of ZrO_2, orthorhombic zirconia (o-ZrO_2), have frequently appeared in the literature [25–33]. This modification can be prepared in two polymorphous types, designated ortho I and ortho II, under high pressures in pure or partially stabilized ZrO_2 (usually Y-ZrO_2).

Orthorhombic zirconia can be prepared in several ways. One of those is transformation of c-ZrO_2 in surface layers of materials exposed to extensive abrasive loading [27], while another is provided by ionic implanting of PSZ or FSZ surfaces [28].

In thin sheets, prepared for studying the structure of the Y-PSZ material by transmission electron microscopy, X-ray diffraction analysis disclosed the presence of o-ZrO_2, formed by transformation of t-ZrO_2, which in turn was created by the effect of etching used in the preparation of the TEM specimens. The t-o ZrO_2 transformation in thin sheets can also be effected by the energy of concentrated electron beams during the actual examination of the material [29]. The o-ZrO_2 modification was also found in a loose, powdered mixture of $Y_2O_3 + ZrO_2$, melted in an electric arc [30].

However, the most frequent reference is made to the preparation of o-ZrO_2 by the HIP technique [31–36]. At temperatures between 400 and 600°C and under pressures exceeding 5 GPa, orthorhombic zirconia, whose parameters are listed in Table III, was prepared by processing fine powdered mixtures of Y-PSZ, containing m- and t-ZrO_2. The o-ZrO_2 always co-exists with t-ZrO_2 and its content corresponds to the decrease of m-ZrO_2 content in proportion to the ratios in the initial mixture. Under the given reaction conditions, t-ZrO_2 is therefore stable [31].

HIP was also used to prepare TZP and PSZ materials in which the o-ZrO_2 was proved to be formed by transformation of t-ZrO_2 by stress-induced conversion following grinding and polishing treatment [32]. The amount of o-ZrO_2 increases with increasing content of the stabilizing addition (Y_2O_3) and with increasing temperature of the HIP process. Heating at 600 – 1000°C will first bring about conversion to m-ZrO_2, and at temperatures of around 1000°C, transformation to t-ZrO_2. The o-m ZrO_2 transformation is martensitic in nature [33].

The data on o-ZrO_2 mentioned so far concern the ortho type I, whose structure is similar to that of m-ZrO_2 and which is formed under pressures of up to about 15 GPa. The ortho II phase, forming under higher pressures, has a structure of the cottunite ($PbCl_2$) type [34, 35]. Its crystallographic parameters are listed in Table III. X-ray diffraction analysis of Y-PSZ prepared under a pressure of 14 to 16 GPa showed that the tetragonal phase in Y-PSZ becomes unstable under these conditions and is transformed

Table III

Density and crystallographic parameters of o-ZrO_2

	Unit	ortho I		ortho II		
		[31]	[33]	[35] 2Y-ZrO_2	[35] 6Y-ZrO_2	[35] 6Y-ZrO_2
Density	g cm^{-3}	6.17	6.08	6.80	6.76	6.68
a	nm	0.505	0.504	0.558	0.558	0.559
b	nm	0.525	0.525	0.333	0.334	0.335
c	nm	0.503	0.509	0.647	0.648	0.649
Elementary cell volume	nm^3	–	0.1346	0.1204	0.1208	0.1213

2Y-ZrO_2 is PSZ with 2 mole % Y_2O_3
6Y-ZrO_2 is PSZ with 6 mole % ZrO_2

to m-ZrO_2. On increasing further the pressure up to 19 GPa, type otho II zirconia is formed [35].

Very recently, experimental evidence was presented on the existence of o-ZrO_2 at atmospherical pressure [36]. The presence of o-ZrO_2 was established in the study of microstructure, mechanical properties and phase composition of Mg-PSZ with a high fracture toughness at very low temperatures. This phase was formed on cooling the material to less than 100°C by transformation of t-ZrO_2 grains. This transformation resulted in worsened mechanical properties and fracture toughness of the material. In the course of heating up, the orthorhombic phase is stable up to 300°C, an increase up to 400°C leads to reconversion to t-ZrO_2 and the properties of the material retain their original values. The existence of o-ZrO_2 at atmospherical pressure was also established in the study of the properties of Y-TZP at temperatures between 100 and 400°C [37].

A more detailed analysis of the transformation processes in ZrO_2, carried out with the use of up-to-date diagnostic techniques, has proved that o-ZrO_2 also exists at atmospherical pressure [36]. Study of microstructure, mechanical properties and phase composition of Mg-PSZ with a high fracture toughness at very low temperatures revealed the presence of o-ZrO_2. This phase was formed by transformation of t-ZrO_2 grains on cooling the material to temperatures below 100°C. This conversion resulted in a worsening of mechanical strength and fracture toughness of the material. On heating up, the orthorhombic phase is stable up to 300°C, further temperature increase to 400°C leads to reconversion to t-ZrO_2 and regaining of the original mechanical properties. Existence of o-ZrO_2 at atmospherical pressure was likewise established during a study of the properties of Z-TZP at temperatures of 100 – 400 °C [37].

A detailed analysis of the transformation processes in zirconia, carried out by the modern diagnostic techniques, established the presence o o-ZrO_2 during stress-induced t-m transformation of ZrO_2 as an intermediate reaction product of this phase conversion. The t-m ZrO_2 process is a two-stage one, the first stage comprising the t-o conversion, the other the o-m transformation [38].

The account given above provides ample reasons for modifying the existing concepts of the polymorphous characteristics of ZrO_2 as well as of the mechanism of the transformation processes taking place during heat treatment of zirconia materials. With respect to the issue of transformation toughening of ceramics by means of ZrO_2, the existence of o-ZrO_2 can be regarded as a factor which in some cases may affect the mechanical characteristics of ZTC materials.

BASIC ASPECTS OF MARTENSITIC TRANSFORMATION AND THEIR APPLICATION TO BRITTLE MATERIALS

Martensitic transformation (MT) is a very important crystallographic process in metallurgy, where it is used to control the mechanical properties of iron alloys. In recent years, this type of phase transformation has also become highly topical in the field of brittle ceramic materials as a means of increasing their resistance to brittle fracture. Analyses of the nature and mechanism of MT with regard to its use in increasing the fracture toughness of ceramics are the subjects of a number of recent studies [e.g. 39–43, etc.] which present concise surveys of the subject matter and some ideas for practical utilization in the field of technical ceramics. One example is MT using the t-m ZrO_2 conversion [19, 22, 24, 39].

MT exhibits some characteristic features:
(1) it is not related to mass transfer by diffusion,
(2) changes in temperature are the driving force of the process,
(3) the particles being transformed change their morphology (the size as well as the shape).

ad (1): MT is neither conditioned on, nor associated to, activated diffusion. Some martensitic reactions take place at low temperatures, sometimes even close to absolute zero. Even under such conditions, martensite is formed readily, the activation energy of the formation and growth of the martensitic phase being virtually zero. MT can likewise be induced by changing the pressure of the system.

In ceramic materials, transformation processes usually take place at high temperatures. In the case of zirconia (the t-m transformation), temperatures of around 1100°C are involved. The process is diffusion-free in nature, the maternal phase and the product having the same composition [19]. The arising phase (m-ZrO_2) is in fact a distorted version of the original structure, as only small changes in the mutual positions of atoms in the original and newly formed lattice occur.

ad (2): In most instances, martensitic transformation is initiated by a change in temperature. At a given temperature, the system contains only a limited number of nuclei capable of being transformed. The changes in volume and shape associated with a change in crystalline structure bring about considerable stresses which, owing to the diffusion-free character of MT, are not relieved by atomic migration. The driving force of transformation are thus changes in temperature (cooling down), in consequence of which new nucleated particles are formed. The transformation reaction is started at a temperature designated M_s (starting temperature of MT).

The M_s temperature is a very significant quantity for the MT process, and its value for a given system is a function of the following factors:
- particle size of t-ZrO_2,
- shape of t-ZrO_2 particles,
- chemical composition of the system,
- external pressure.

ad (3): the change in particle morphology is a typical aspect of the MT process, and simultaneously an advantageous identification criterion for determining the character of transformation reactions. The martensitic-type reactions are associated with the occurrence of a shear stress in the discrete volume of the material, brought about by changes in the shape of the particles.

For a given composition of the system, there hold defined and constant relations between the original and the newly formed phase, which is situated around the habit plane, common to both phases, in the form of plate-shaped particles of the product of martensitic transformation.

The most recent findings in the field on MT in ceramic systems containing ZrO_2 have provided some new aspects of the mechanism of this type of phase conversion [29, 44, 45, 46]. During a study of MT brought about in thin Y-TZP sheets by the energy of the electron beam, t-m ZrO_2 MT was found to show a certain degree of reversibility. This is caused by partial transformation of t-ZrO_2, involving formation of mechanical stresses acting against the effects of external forces, which are the driving force of the transformation process. A reversible t-m conversion is likewise exhibited by Mg-PSZ under compressive stressing of the material.

A detailed study of a group of Mg-PSZ materials with a great fracture toughness (8 - 14 MPa $m^{1/2}$) showed that to suppress the phenomenon, it is necessary to ensure conditions for stabilizing the transformation product in the surface layers of the materials, where the tendency towards a reversible m-t process is most distinct [49].

Such conditions are provided by high tensile (>359 MPa) or compressive (>1200 MPa) stresses, which in certain suitably oriented crystals, are responsible for the formation of "bands" containing mostly transformed particles. These bands represent a barrier against the reversible transformation process. Their existence is conditioned on the presence of nuclei containing satisfactory amounts of neighbouring transformed particles, which act as an autocatalyst for the formation and growth of the transformation band.

Stabilization of the t-m transformation product is also contributed to by relieving the stress arising during t-m conversion in PSZ and TZP materials, which usually get into the state of thermoelastic equilibrium. This stress acts against further course of transformation, and in the absence of external forces would lead to the reversible m-t process. The stresses are relieved either in consequence of microcracking during formation of m-ZrO_2 as the conversion product, or by twinning of m-ZrO_2 particles.

PHYSICO-CHEMICAL ASPECTS OF TRANSFORMATION TOUGHENING OF CERAMICS WITH ZIRCONIA

Transformation toughening is the so far most effective tool in the preparation of ZTC ceramics with a high fracture toughness. If dispersed or precipitated ZrO_2 in the ceramic matrix is to play the role of an

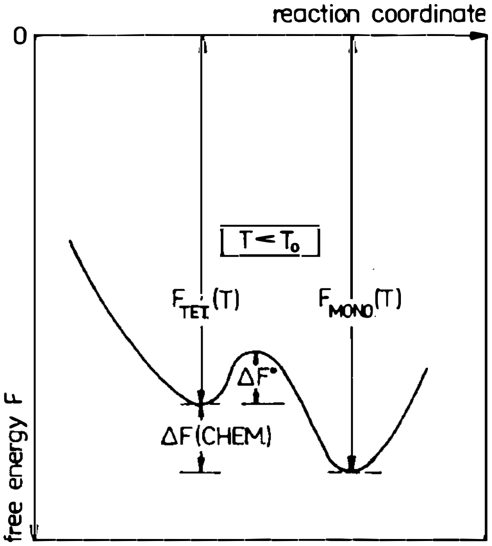

Fig. 5. Energy aspects of t-m ZrO_2 phase transformation for an isolated particle [50].
T_0 - the temperature at which both t and m ZrO_2 have the same free energy,
T - the actual temperature.

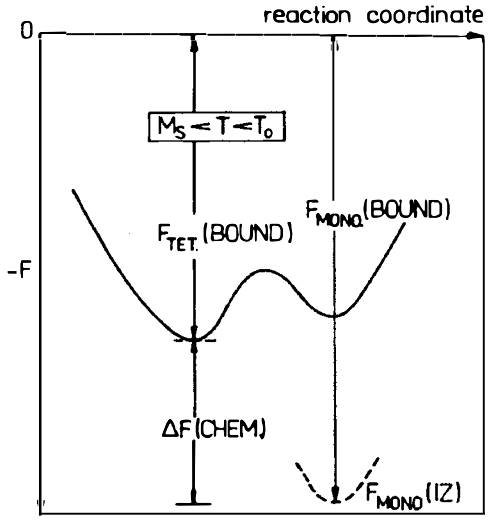

Fig. 6. Energy aspects of t-m ZrO_2 phase transformation for a particle bound in a strong matrix [50]. T_o - the temperature at which both t and m ZrO_2 have the same free energy,
T - the actual temperature.

active factor in the toughening process, the spontaneous t-m transformation in the preparation of the material or product must be suppressed to the maximum possible degree. Under normal conditions, this spontaneous transformation takes place on cooling the system below approx. 1000°C. The t-ZrO_2 grains remaining in the matrix after cooling below the transformation temperature can be regarded as crystals in the state of a metastable equilibrium [10]. With respect to their transformation temperature M_s, which under the new conditions is lower than room temperature, the t-ZrO_2 grains are in fact in a stable state, except for the region in the neighbourhood of the crack front, where a high stress concentration leads to transformation to m-ZrO_2.

The issue of t-ZrO_2 stability in the ceramic matrix is analyzed in detail in [47], where the thermodynamic, nucleation, chemical and energy aspects of the t-m ZrO_2 phase transformation are discussed.

The thermodynamic conditions of this transformation for an isolated or bound t-ZrO_2 particle are illustrated by Figs. 5 and 6.

In the case of an isolated particle (Fig. 5), its thermodynamic stability increases with decreasing free energy of the system (the same obviously applies to the system with bound t-ZrO_2 particles). However, to implement the t-m phase transformation, one has to overcome the nucleation barrier ΔF^*. The total free energy released during the phase transformation is ΔF_{Chem}.

The differences in the thermodynamic aspects of transformation of a free particle and one bound in the matrix, indicated in Figs. 5 and 6, can be characterized as follows:

- the free energy of a bound t-ZrO_2 particle, F_{TET} (BOUND) may differ considerably from the free energy of an isolated particle, F_{TET} (IS). This is due to the differences in the dilatation properties of the particle and of the matrix, responsible for the creation of stresses, as well as to other factors, brought about by diffusion of mass in the system during its preparation at relatively high temperatures.

- the nucleation energy, F, need not be the same in the two instances being discussed. It depends on the character of distribution of the t-ZrO_2 particles. In the case of coherent, precipitated particles, or intragranularly localized t-ZrO_2 (PSZ), the surface nucleation to m-ZrO_2 is quite energy-consuming, so that the ΔF^* value is rather high. In contrast to this, in the case of an intergranular sintered t-ZrO_2 particle (such as in ZPA composites), the nucleation of m-ZrO_2 is easier and the ΔF^* barrier is thus lower.

- the difference in free energies F_{mono} (BOUND) and F_{mono} (IS) is a decisive thermodynamic factor for realization of the t-m transformation (cf. Fig. 6). Transformation of t-ZrO_2 in solid matrix leads to an increment of mechancal stresses in the system, which, when exceeding the driving force of the process, i.e. ΔF_{Chem}, resist the phase transformation and the t-particles become stable with respect to conversion. To achieve the transformation, the system has to be cooled below the M_s temperature, where the spontaneous t-m transformation is started.

On the basis of experimental results aimed at determining the effect of surface energy and internal stress energy on the relation between M_s and particle size of t-ZrO_2 particles, it was concluded that these energy aspects have no effect on the given relationship. This finding can be regarded as holding generally for all ZTC materials [47], although some studies ascribe, in certain specific instances, a great significance to the effect of surface energy and internal stress on the dependence of M_s on particle size [42, 48, 49].

Papers dealing with the nucleation aspects of t/m transformation emphasize the important effect of the nucleation process on the stability of t-ZrO_2 particles in PSZ and ZTA materials, even though the concepts of the process mechanism and kinetics differ. Some authors [50] assume that the transformation is conditioned on the presence of martensitic nuclei formed in the material during its preparation. Another theory assumes existence of martensitic nuclei at the t-ZrO_2/Al_2O_3 matrix contact areas (in the case of ZTA ceramics) or the t-ZrO_2/m-ZrO_2 matrix one (in that of PSZ materials) [47]. With PSZ, a significant role is placed by the character of t-ZrO_2 precipitated in the matrix of the material [51, 52].

Assessment of the effect of chemical aspects on the t-m ZrO_2 transformation is difficult owing to the relatively limited knowledge of the chemism in the system Al_2O_3-ZrO_2. The solubility of Al_2O_3 in ZrO_2 was generally considered to be very poor. However, with the use of modern analytical methods (EDAX, EELS) it was recently proved to amount to up to several percent [47]. It is assumed that the chemical properties of ZrO_2 particles depend on their size, and from this follows a probable effect of chemical factors on M_s and thus also on the stability of t-ZrO_2 in PSZ or Al_2O_3-ZrO_2 materials. However, this effect is generally assumed to be less significant compared e.g. to the nucleation aspects of the t-m transformation.

ZTC MATERIALS

Classification of ZTC materials

Development of ceramic materials with an elevated resistance to brittle fracture and improved mechanical strengths has brought about a number of new materials of diverse chemical compositions, microstructure, preparation technology and application possibilities. The character of their microstructure appears to be the most convenient criterion for their classification, owing to the narrow connection between the mechanical properties, which are the focal point of interest of ZTC ceramics, and their structure. This classification was suggested by Claussen [12], who divided ZTC materials into three basic categories (Fig. 7):

A – materials based on PSZ
B – materials containing dispersed ZrO_2
C – complex ZrO_2 systems.

Each of these categories contains six structural types of ZTC materials. Some of them are already commercially produced, others are in the stage of development, and some types in category C indicate the probable trends of future development in the field of ZTC ceramics.

Category A includes PSZ materials with various stabilizing additives (Y_2O_3, CaO, MgO, CeO_2 and some other rare earth oxides). In term of the initial raw materials, the working mix preparation procedures and ways of their processing, various structural types of ZrO_2 (PSZ) materials arise, involving stress-induced transformations (A1, A2, A3, A6), microcrack nucleation (A4) and combinations of these mechanisms (A5) as the toughening mechanisms.

Tetragonal polycrystalline ZrO_2 (TZP, type A3) of fine-grained structure (0.1 – 1.0 μm), with high mechanical strength (600 – 700 MPa) and fracture toughness (15 – 20 MPa $m^{1/2}$) is the most interesting material in category A. It is prepared from Y-PSZ (Y_2O_3 content 2 – 3 mole %) at 1400°C [11].

Category B comprises materials containing zirconia particles dispersed throughout their matrix (other than of ZrO_2). Also here, the two basic mechanisms of transformation toughening may be utilized to increase mechanical strength and toughness of the materials. At present, materials with an alumina-based matrix, designated ZTA ceramics, belong among the technologically most advanced ones. They have been prepared in virtually all of the structural B1 – B6 types, and some of them are already included in the manufacturing programmes of the foremost world manufacturers of technical ceramics.

As already mentioned, category C materials are all development types which in some cases represent trends that the transformation toughening techniques will use to produce a new generation of structural ceramics. These are model materials whose lists are far from complete, and are going to be supplemented with additional structural types in the course of advancing development.

ZTA MATERIALS AND SOME TECHNOLOGICAL ASPECTS OF THEIR PREPARATION

Zirconia-toughened alumina belongs among the materials which, in addition to PSZ ceramics, find ever more extensive application in technological practice as new structural materials with superior performance properties.

The basic raw materials for ZTA ceramics are usually products of special processes of the so-called qualified chemistry. This has been increasingly producing powders with precisely specified properties, in particular chemical composition, granulometry, and in the

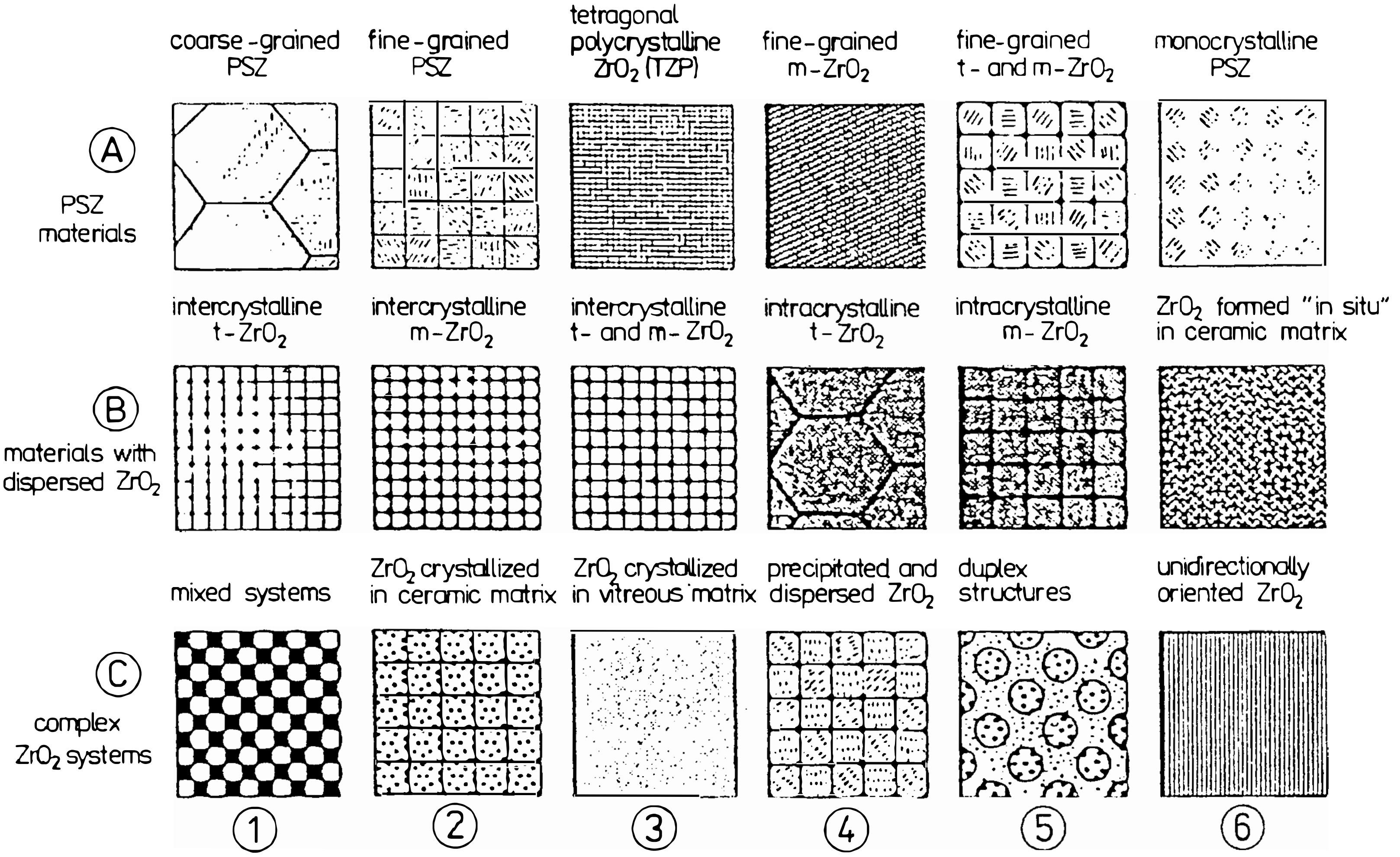

Fig. 7. Structural types of ZTC materials after Claussen [12].

Table IV

Selected properties of powdered PSZ made by TOYO SODA [73] and the respective PSZ ceramics

	PSZ powders					
	2Y	3Y	4Y	9Mg	12 Ce	Super Z
Stabilizing additive	Y_2O_3	Y_2O_3	Y_2O_3	MgO	CeO_2	Y_2O_3
Content of stab. additive (mole %)	2	3	4	9	12	4.3
d_{50} [μm]	0.3	0.3	0.3	0.3	0.3	0.3
Apparent density after firing [g cm^{-3}]	6.07	6.05	6.03	5.60	6.00	5.50
Bending strength [MPa]	1300	1200	1000	500	500	2400
K_{IC} [MPa m$^{1/2}$]	10	8	7	9	20	6

case of ZrO_2, with a well defined phase composition and content of mineral admixtures (e.g. Y_2O_3, MgO, CeO and some other oxides).

There is a number of world manufacturers who supply special types of alumina and zirconia for the preparation of various ceramic materials, among others also ZTA ceramics.

For example, the Japanese Toyo Soda company [53] manufactures, by the so-gel process, a wide assortment of powdered ZrO_2 with submicron particle size, containing 2 to 8 mole % Y_2O_3, also Mg-PSZ with 9 mole % MgO, and Ce-PSZ with 12 mole % CeO_2. For the HIP technology, the company supplies the Super-Z powder, a hybrid product having the composition

ZrO_2	75.7 wt. %
Al_2O_3	20.0 wt. %
Y_2O_3	4.3 wt. %

Following the appropriate processing, the powdered materials yield PSZ and ZTA materials with superior mechanical properties and fracture toughness, as follows from Table IV.

The British Unitec company is a significant European producer of powdered zirconia for structural technical ceramics. It has developed the so-called electrorefining technology of ZrO_2 preparation, which yields reactive PSZ powdered materials of various types (Ca-, Y-, Mg-, Ce-PSZ), as well as a fine-grained monoclinic ZrO_2 (mean grain size $d_{50} = 0.6\ \mu$m), suitable for the preparation of high-strength ZTA ceramics (up to 800 MPa) with a high fracture toughness (of up to 20 MPa m$^{1/2}$) [54, 55]. Other major manufacturers of powders for ZTA ceramics include MEL in Great Britain, Zirconia Sales Ltd. in Great Britain. Criceram in France, TAM Ceramics Inc. in the USA, and some others. In view of the exacting technological demands on zirconia raw materials for the field of advanced ceramics, their prices are of the order of a thousand Czech Crowns per kilogram.

Alumina for ZTA ceramics must meet the requirements for high purity and reactivity at relatively low sintering temperatures (14 to 1600°C). Preferred are fine-grained powdered materials supplied by firms Baikowski France, Martinswerk FRG, Criceram France, or some types supplied by Alcoa. Their prices are in the range of CC 500 to 1000 per kilogram. Of local resources, use can be made, with certain reservations (lower purity, less suitable physical properties), of alumina from Spolchemie Ústí nad Labem, whose present price is CC 220 per kg. However, the raw material is in its low-temerature gamma form, and for ceramic purposes has to be calcined to convert it to its alpha modification.

Table V presents a schematic diagram of the technology of ZTA materials. In the field of forming processes of the working mixes for ZTA ceramics, use is often made of piston and isostatic pressing, or isostatic pressing under high pressures (300 to 800 MPa) [59, 60, 61, 62] followed by plain sintering at 1400 to 1600°C. This heat treatment is also used for semiproducts prepared by extrusion of plasticized materials based on Al_2O_3 - ZrO_2 [63, 64]. Experiments were also carried out with forming the materials by explosion under pressures of up to 100 GPa and temperatures of 500 to 1000°C [65]. Use is frequently made of hot pressing [47, 66, 69] and the HIP technique combined with some pressing method [59, 60, 64].

An interesting contribution in the field of the ZTA materials technology with respect to their mechanical properties, particularly their fracture toughness and Young's modulus, is provided by their heat treatment in a reduction atmosphere [70, 71]. This process succeeds in retaining in the matrix higher proportions

Table V

Schematic diagram of ZTA ceramic technology

Initial raw materials	Al_2O_3 ZrO_2 Zr compounds Al_2O_3 + ZrO_2 hybrid powders
Preparation of working mixes	dry homogenization of powders precipitation co-precipitation sol-gel processes freeze-drying
Forming	piston pressing CIP extrusion
Heat treatment	bisque firing plain sintering pressure sintering HIP sinter HIP
Mechanical working	grinding lapping polishing
Evaluation of properties	apparent density water absorption σ_f K_{IC} Weibull's modulus

Table VI

Some properties of ZTA materials sintered in air atmosphere and in non-oxidating hydrogen atmosphere [71]

Property	Heat treatment	
	Oxidating atmosphere	Hydrogen atmosphere
K_{IC} (MPa $m^{1/2}$)	6.3 ± 0.3	8.2 ± 0.2
Content of t-ZrO_2 (wt.%)	44	55

of t-ZrO_2, thus improving the fracture toughness, as indicated by Table VI.

Use of these modern technological methods often results in the preparation of materials with superior properties. However, the manufacturing costs of the ZTA ceramics also rise significantly. It is therefore useful to follow some traditional and known technological procedures used in particular in the field of oxide ceramics e.g. corundum, and to assess their viability in the technology of ZTA materials.

Comparatively little attention has so far been paid to the preparation of ZTA ceramics based on plain sintering of compacts prepared by piston or isostatic pressing of alumina-zirconia mixtures. The forming of submicron powders involves considerable difficulties, especially when using piston pressing, owing to their extremely fine granulometry. However, a solution has recently been found, e.g. for processing submicron powdered corundum by piston and isostatic pressing [72]. Application of the methods to fine-grained hybrid alumina-zirconia powders has brought very promising results with respect to both the processing technology and the properties of the products [72].

CONCLUSION

The field of ZTC materials has undergone a dynamic and successful development during the fifteen years since the first reports on the possibility of suppressing the brittleness of ceramic materials appeared. A number of new ceramic materials suitable for structural applications in many fields of technology have been devised. In the course of development of these materials, the principles of transformation toughening were discovered and verified, the technology of preparation of various suitable initial powdered materials mastered, various technological variants of ZTA and PSZ ceramics worked out, and methods for evaluating their properties devised and standardized.

Despite the significant progress achieved during the relatively short time, ZTA and PSZ ceramics have not yet found massive application as structural materials. This is due to their relatively low reliability caused by the complexity of their technology, and the subsequent poor reproducibility of their properties. Moreover, there is also the problem of a certain degradation of mechanical properties of some ZTA and PSZ types occurring at elevated temperatures, which restricts their high-temperature applications. The high prices of the materials are another factor limiting their wider technological utilization. The extensive development now under way in the field of ZTC ceramics is aimed above all at studying and eliminating these limiting factors. As soon as the problems in question are mastered, technological practice will have at its disposal ceramic materials which will significantly widen the assortment of materials for demanding structural applications.

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Translated by K. Němeček

Book Reviews

PROCEEDINGS OF THE FIRST INTERNATIONAL CONFERENCE ON TRANSPORT PHENOMENA IN PROCESSING, March 22-26, 1992, Honolulu, Hawaii

Editet by Selçuk I. Güçeri
Sponsored by National Science Foundation (U.S.A.), Lord Corporation (U.S.A.), Teijin Limited (Japan), The Dow Chemical Company (U.S.A.), ALCOA (U.S.A.)
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The book contains 129 contributions covering the following 21 thematic items:

1. Crystal Growth (8), 2. Chemical Vapor Deposition and Infiltration (6), 3. Melting Solidification: Process Modelling (10), 4. Melting Solidification: Process Simulation (7), 5. Material Removal (6), 6. Forming: Rolling, Sheet Forming, Forging, Extrusion (12), 7. Welding (4), 8. Surface Heat Transfer in Materials Processing (5), 9. Natural Convection in Materials Processing (4), 10. Non-Newtonia and Viscoelastic Flows (6). 11. Two-Phase Flow and Suspensions (6), 12. Electromagnetic Effects in Material Processing (4), 13. Polymer Extrusion (6), 14. Physico-chemical Issues in Polymers (3), 15. Injection Molding (9), 16. Resin Transfer Molding and Impregnation of Fibers Preforms (8), 17. Composites (6), 18. Materials Processing with Lasers (4), 19. Ceramic and Glass (4), 20. Thin-Film and Membrane Technology (3), 21. Special Topics (8).

A trait common to most of the contributions is, that they emphasize the importance of solving processes connected with the formation of materials in relation to the emerging microstructures and their corresponding properties; in this sense they represent a transition from a merely experimental to a more quantitative description on the basis of mathematic modelling.

The respective models start from rational thermodynamics or, more often, directly from transport equations for mass, heat and momentum and are solved mainly by the finite elements method.

The survey of the thematic range given above demonstrates the importance of these newly edited proceedings, that give an insight into the wide spectrum of processes solved in the field of material science and material engineering, applicating a modern modelling approach.

The contributions are written on a highly theoretical level and should be equally inspiring for planning pre- and postgraduate teaching of specialists in both polymere and inorganic - metallic as well as non-metallic - materials.

Taking into account the brilliant reproduction and the appealing layout of each article, we may say, that the book is an excellent contribution to the literature specialized on material science and material engineering. All experts interested in modern approaches how to solve processes exactly, control and optimalize them, as well as preparation of materials with required predictable and reproductable properties, should find important informations in this book.

The interest of leading institutions and firms of the world sponsoring the conference is further evidence of the important role that plays this modern approach of technical chemistry for solving problems of material research and its irreplaceable function as far as the development of new materials is concerned. It may be hoped, that conferences on this subject will continue.

Jiří Havrda

ENCYCLOPEDIC SURVEY OF MINERALS, J. H. Bernard, R. Rost et al., ACADEMIA Prague, Prague 1992, 1st edition, 704 pages, 484 figures, 32 pages of art paper annexes.

The book presents essential diagnostic data on all minerals, using their nomenclature valid till 1992. It is intended for mineralogists, geologists and advanced laymen who need the data for at least informative determination and classification of minerals.

The minerals are dealt with in an alphabetical order (more than 3,305 items). The following characteristics are given for each mineral: Name of the mineral, designation of the origin of its name, the current synonyms and varieties, the chemical formula, classification in the Strunze system, the crystal system, the spatial group, lattice parameters, the strongest diffraction lines, macroscopic appearance, hardness, density, microscopic data on transmitted and reflected light, microhardness, other outstanding physical or chemical properties, paragenesis and localities of occurrence, references, designation of abundance or rarity of the mineral, and finally the authors' initials.

In the systematic classification of mineral species, use is made of the so far the best and generally employed Strunze system of 1982, based on a suitable combination of structural and chemical criteria. For the purpose of ready orientation, the authors have introduced a numerical hierarchic coding system. From the fifth class, they have separated borates as an independent sixth class, after which follow sulphates (7), phosphates (8), silicates (9) and organic compounds (10).

This being an extensive publication, the reader should first become acquainted with the rules used in setting up the book and should read the instructions for use, because even less usual abbreviations and formulas are employed in the text.

The updated maps of mineral occurrence localities are very valuable.

The book can be recommended to those dealing with the determination of minerals (assessment of raw materials, inhomogeneities in products, etc.) and all those who need basic information on various minerals and should like to have it within reach.

Martin Maryška

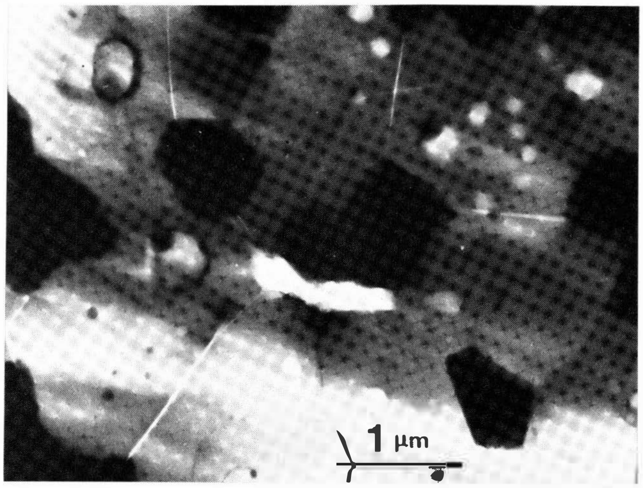

Fig. 2. The microstructure of ZTA material with cracks nucleated by t-m ZrO_2 transformation [11].