

Effect of zirconia (3 mol% yttria) additive on mechanical properties and structure of alumina ceramics

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The effects of ZrO_2 -3 mol% Y_2O_3 additives containing 7.3, 15, 23.3 and 32 vol% of ZrO_2 on σ_f , K_{Ic} , H_V and the microstructure of hot-pressed alumina-based ceramics were investigated. The presence of the m-, t- and t'- ZrO_2 phases was discovered by using X-ray diffraction and transmission electron microscopy. An inhomogeneous distribution of Y_2O_3 in the ZrO_2 grains was observed. The variation of the mechanical properties of the ceramics is explained by the influence of different toughening mechanisms and by a change in the structure of the material.

1. Introduction

Alumina-based ceramics are used as tool and engineering materials but low mechanical properties limit their application. Mechanical properties such as the bending strength σ_f and fracture toughness K_{Ic} considerably increase with the addition as a secondary phase of partially stabilized ZrO_2 [1]. However, improvement of the mechanical properties in this case is achieved by a choice of more expensive methods of producing highly dispersed and homogeneous mixtures (chemical methods) and by using hot isostatic pressing instead of sintering. Hot pressing of high-strength ceramics is of specific interest since in some cases the requirements to the batch can be reduced. Investigations done by the present authors [2] showed that Al_2O_3 - ZrO_2 composites having relatively high property levels ($\sigma_f \approx 900$ -1000 MPa and $K_{Ic} \approx 8$ MPa m^{1/2}) can be produced by HP; it is therefore possible to improve the fracture toughness and strength without a dominant mechanism of transformation toughening.

2. Experimental procedure

The effect of ZrO_2 -3 mol% Y_2O_3 additives containing 7.3, 15, 23.3 and 32 vol% ZrO_2 on σ_f , K_{Ic} , H_V and the microstructure of hot-pressed alumina-based ceramics was investigated in this work. The composites were prepared in the following way: the raw commercial powders, some properties of which are shown in Table I and which are described in detail elsewhere [3], were mixed in appropriate ratios in a ball mill in an acetone medium for 24 h to a dispersion $d_{50} = 1.1$ μ m, then dried and hot-pressed for 1 h at $T = 1650$ °C, $P = 25$ MPa. The strength was measured by the three-point bend method with 20 mm

span and a crosshead speed of 2 mm min⁻¹ (size of the sample 5 mm \times 5 mm \times 35 mm). After polishing the specimens were tested for K_{Ic} and H_V by the indentation method at a load of 500 N. The phase analysis was performed by X-ray diffraction (CuK_α radiation). The primary curve processing (separation of superimposed peaks and definition of curve parameters by position, width and shape) was performed by the least-squares method [4]. The ZrO_2 contents of different crystalline phases were measured according to Miller *et al.* [5].

3. Results and discussion

Numerous publications (e.g. [6, 7]) have shown that an increase of the amount of ZrO_2 (Y_2O_3) additive in alumina leads to increasing strength and toughness, suggesting toughening by the phase transformation mechanism; an external applied load can cause a phase transformation of ZrO_2 from the tetragonal (t) to the monoclinic (m) phase by a process involving energy absorption. The action of this mechanism is supported by a considerable increase of m- ZrO_2 on the fracture surface as compared with the amount present in the volume (i.e. on a polished surface). ΔC_m is equal to $\sim 50\%$ [8]. It is known that the active component for phase transformation is t- ZrO_2 with a low content of the stabilizing Y_2O_3 additive, in contrast to the so-called t- ZrO_2 phase also present in the composition range from 2 to 14 mol% $YO_{1.5}$, where the amount of Y_2O_3 is rather higher in t'- ZrO_2 than in t- ZrO_2 . The phase stability (transformation capability) of these phases depends on their tetragonal regularity (ratio c/a) [9]. Fig. 1 shows the X-ray image taken in the doublet region $(004)_t$ - $(400)_t$ - ZrO_2 on the polished surface of an Al_2O_3 -23.3 vol% ZrO_2

TABLE I Powder characteristics

Powder	Specific surface ($\text{m}^2 \text{g}^{-1}$)	Phase composition	Additive (wt %)				Agglomerate size (μm) ^a
			SiO ₂	TiO ₂	MgO	Fe ₂ O ₃	
Al ₂ O ₃	4.5	α	0.045	0.0017	0.02	0.01	2.5
ZrO ₂	20	m	0.030	0.001	0.06	0.004	11

^a Measured by Laser Micron Sizer.

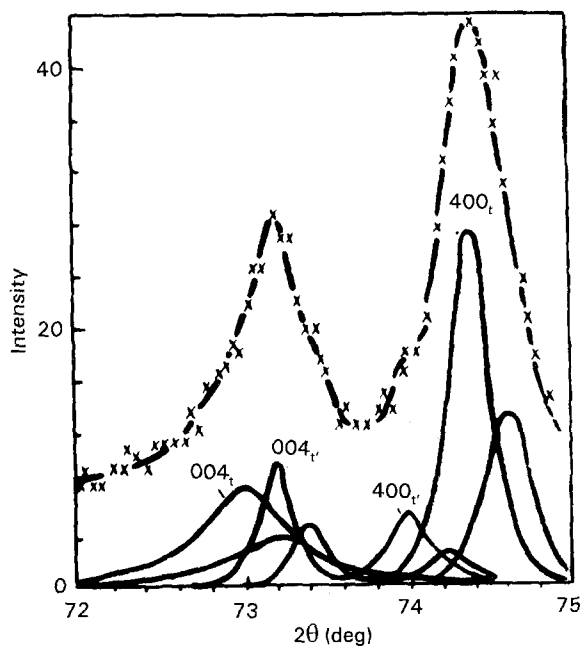


Figure 1 Results of X-ray diffraction analysis at the doublet (004)_t-(400)_t-ZrO₂ on the polished surface of Al₂O₃-23.3 vol % ZrO₂ (3 mol % Y₂O₃) ceramic.

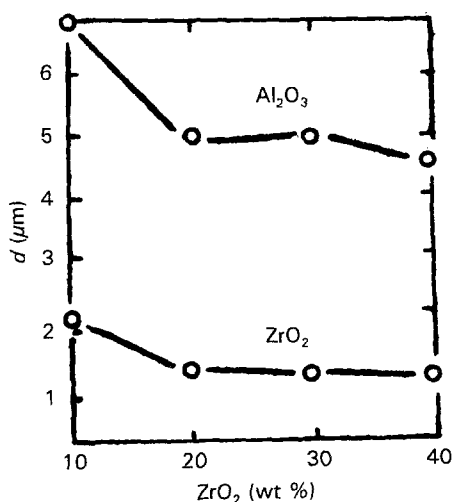


Figure 2 Relationship between the sizes of Al₂O₃ and the ZrO₂ grains and the amount of added secondary phase.

(3 mol % Y₂O₃) ceramic. As shown in this figure, there are two tetragonal phases: the t-phase with parameters $a = 0.5092 \text{ nm}$, $c = 0.5176 \text{ nm}$, $c/a = 1.0165$ and the t'-phase with parameters $a = 0.5166 \text{ nm}$, $c = 0.5164 \text{ nm}$, $c/a = 1.0094$.

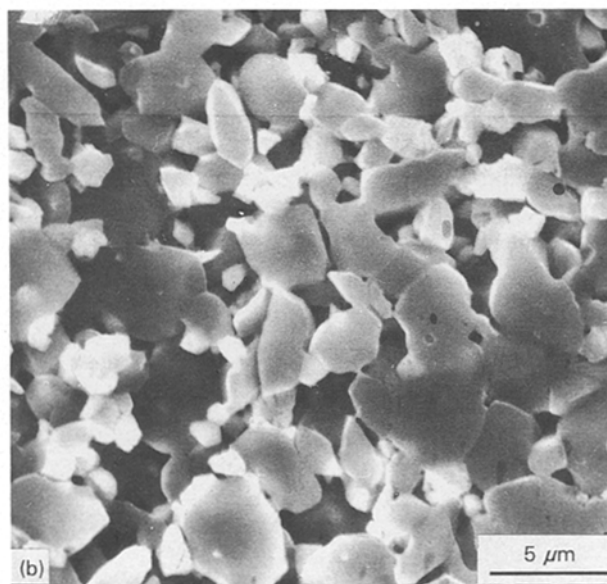
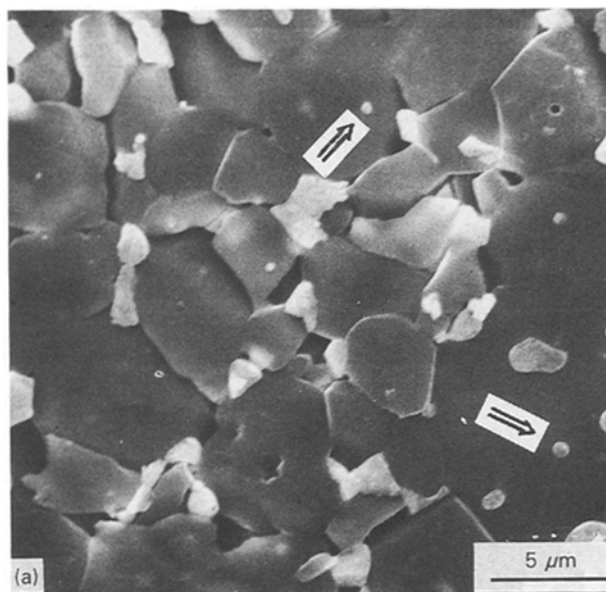


Figure 3 Structure of hot-pressed ceramics of the following compositions: (a) Al₂O₃-7.3 vol % ZrO₂ (3 mol % Y₂O₃) (the arrows indicate intragranular particles of ZrO₂), (b) Al₂O₃-23.3 vol % ZrO₂ (3 mol % Y₂O₃).

3.1. Microstructure

Examination of the microstructure of these ceramics shows that the addition of 7.3 vol % ZrO₂ does not sufficiently slow down alumina grain growth, but more ZrO₂ additive allows the development of more

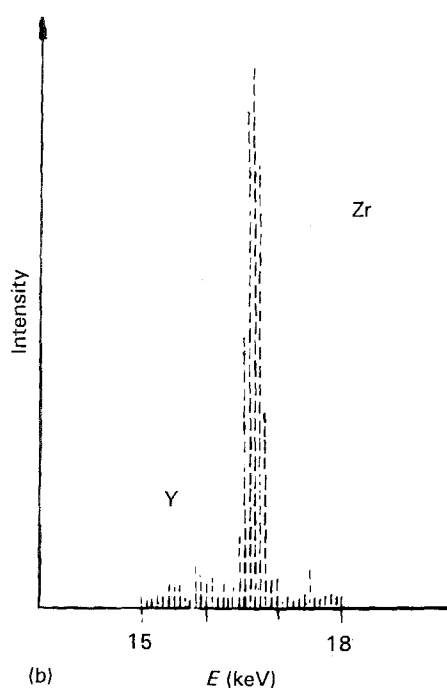


Figure 4 (a) Microphotograph of m-ZrO₂, (b) results of X-ray microanalysis of the m-ZrO₂ particle.

fine-grained ceramics (Figs 2, 3a and 3b). The microstructure of Al₂O₃-7.3 vol % ZrO₂ comprises great quantities of fine-grained ($\leq 0.5 \mu\text{m}$) spherical or ellipsoidal ZrO₂ particles entrapped inside as a result of Al₂O₃ grain recrystallization [10]. However, with increase of the total ZrO₂ amount the ZrO₂ grains are disposed as a rule in the form of coarser (0.5–1.5 μm) angular-shaped irregular particles distributed along the boundaries, on the junctions of three or four neighbouring grains.

TEM and EDAX examination of the structure and chemical composition of ZrO₂ grains revealed two groups of particles. The first group is m-ZrO₂ particles containing 0.5–1.0% (by weight) Y₂O₃ and having a twin structure with lamellae thickness of 0.5 μm (Fig. 4a and b). The second group is t-ZrO₂ and t'-ZrO₂ particles (formed as a result of c-ZrO₂ displacement phase transition) containing a higher amount of a stabilizing additives in solid solution (4.5–7.0 wt %) and having structures of different types: modulated "tweed" contrast regions (Fig. 5b and c);

grains with microirregularities (Fig. 5d and e) which can be associated with the above-mentioned phases [11, 12]. The differences in the content of Y₂O₃ in the ZrO₂ grains can be explained by the specific processes of preparing the mixture (mechanical mixing) and HP which do not achieve a homogeneity of distribution of Y₂O₃ as good as that of a solution method. The degree of homogeneity of the distribution depends on the time and the temperature of HP, and the size of the ZrO₂ particles determines the diffusion of yttrium because Y₂O₃ does not form a solid solution in ZrO₂. The volume diffusion coefficient of yttrium is very low

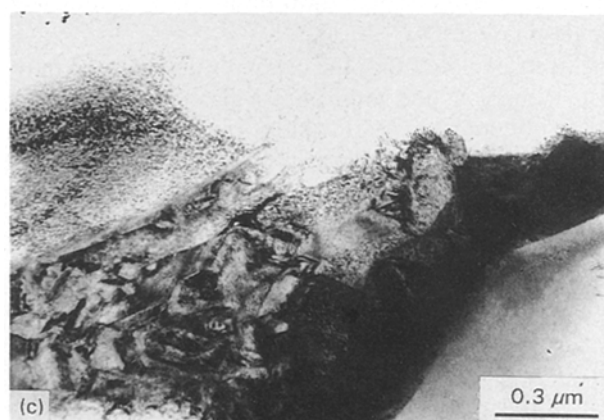
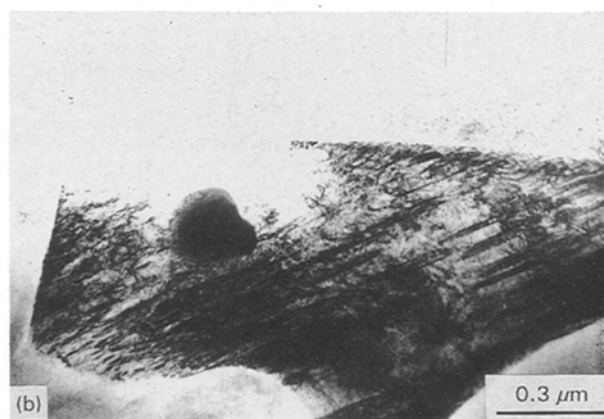
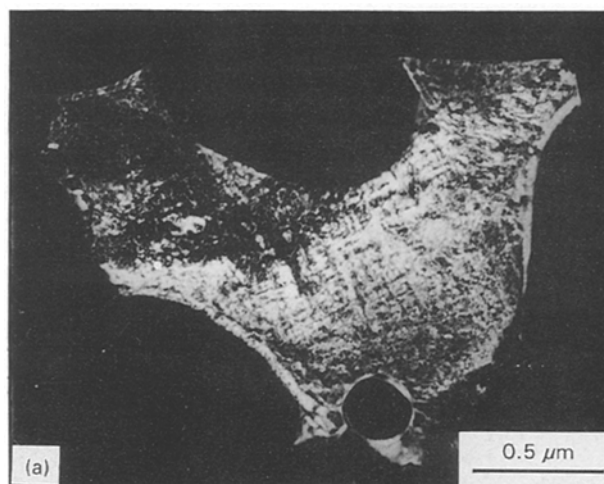


Figure 5 Microphotographs and X-ray diffraction microanalysis of t- and t'-ZrO₂ particles: (a) "tweed" contrast, (b) aggregate-like precipitates, (c) 90° twin lamellae, (d) microinhomogeneities, (e) X-ray diffraction microanalysis of the particle in 5(d).

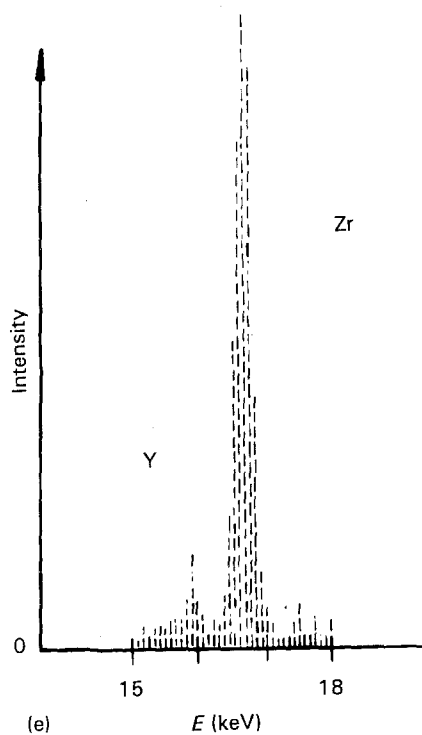
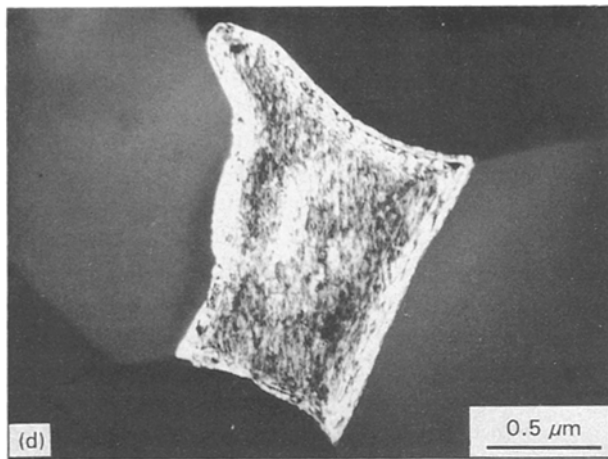


Figure 5 (continued).

and equal $10^{-14} \text{ cm}^2 \text{ s}^{-1}$ at 1400°C [13]. Therefore in spite of a high heating rate and short-time HP, treatment at 1650°C could not result in a completely single-phase ZrO_2 .

It is to be noted that the ceramics investigated may also include a fine amorphous glassy phase in the grain boundaries. As a whole, the structure of as-received ceramics is characterized by a considerable microinhomogeneity and heterophase condition, which may be interesting with respect to the initiation of energy dissipation processes in crack tips with increasing toughness.

3.2. Mechanical properties

The concentration relations of hardness, fracture toughness and strength of the ceramics are shown in Fig. 6. The toughness hardly changes in the concentration range of ZrO_2 from 0 to 33 vol %, in contrast

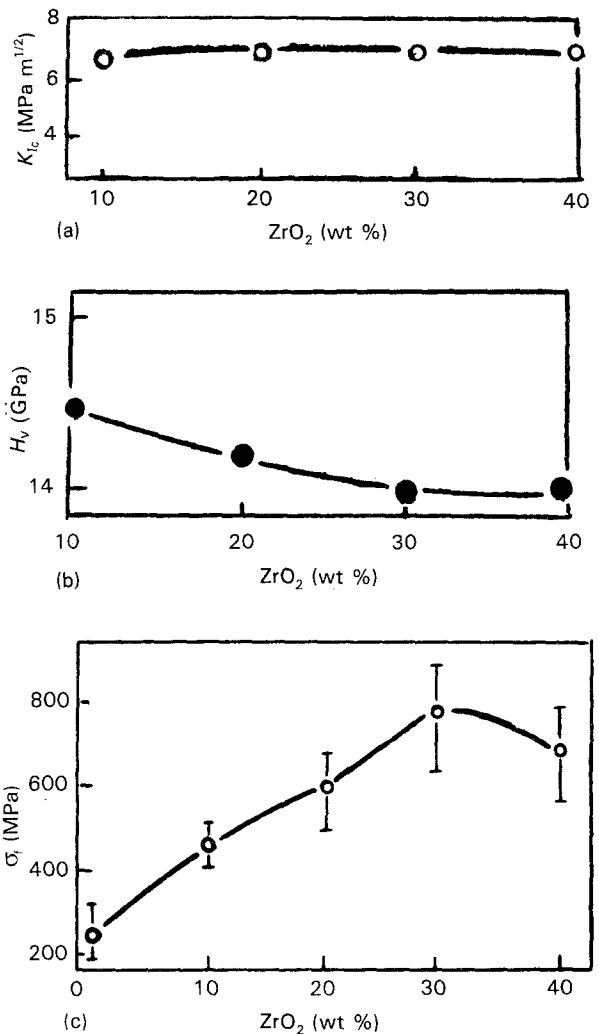


Figure 6 Concentration dependences of (a) fracture toughness (K_{Ic}), (b) hardness (H_v) and (c) strength (σ_f) of Al_2O_3 - ZrO_2 (3 mol % Y_2O_3) ceramics.

TABLE II m- ZrO_2 content in Al_2O_3 - ZrO_2 (3 mol % Y_2O_3) composites

ZrO_2 (3 mol % Y_2O_3) in Al_2O_3 (wt %)	m- ZrO_2 (wt %)		ΔC_m (wt %)		
	Polished surface	Ground surface	Fracture surface	Ground surface	Fracture surface
10	16	28	30	12	14
30	20	23	24.55	3	4.55
40	22	22	24	0	2

with ceramics with unstabilized ZrO_2 in which there is a clear maximum at 10–13 vol % as a result of transformation toughening [14]. In this case the gain in fracture toughness is the result of the effect of several processes: coarsening of a fracture surface caused by a crack bending round the obstacles (ZrO_2 particles); t-m- ZrO_2 phase transformation microcracking. Fractographic analysis shows that the coarseness of the fracture surface changes slightly with varying ZrO_2 content and the effect of crack bending round the obstacles for fracture toughness should be con-

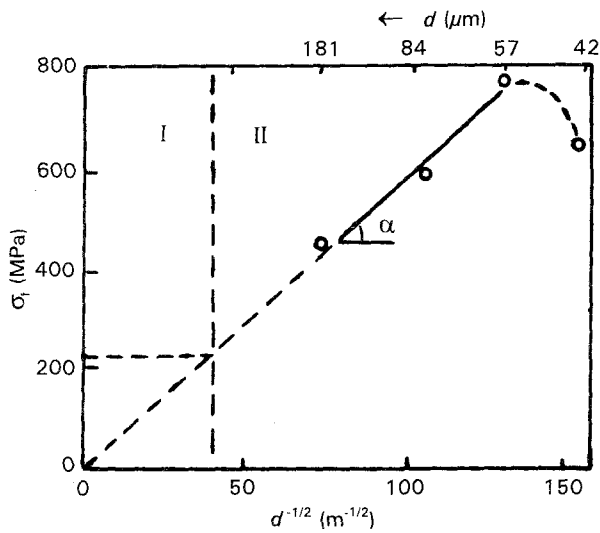


Figure 7 Dependence of $\text{Al}_2\text{O}_3\text{-ZrO}_2$ (Y_2O_3) ceramic strength on distance between second-phase particles. Straight line represents $K_{Ic} = 1.23 \tan \alpha \approx 7.2 \text{ MPa m}^{1/2}$.

stant. The phase transformation contribution is small with the addition of 7.3 vol % ZrO_2 and decreases to zero at 32 vol % ZrO_2 (Table II). The total toughness increase may remain constant with addition of ZrO_2 in the investigated range, as one can observe.

A slight concentration dependence is also observed for hardness although with added ZrO_2 $H_v \approx 13 \text{ GPa}$, which is much lower than that of Al_2O_3 ($\sim 19 \text{ GPa}$).

The constant behaviour of hardness suggests that its value as well as in other ceramic materials [15] is determined by toughness and strength and not by ductility. At the same time, the strength drastically increases from ~ 200 to $\sim 800 \text{ MPa}$ (Fig. 6). Such a strength increase at constant fracture toughness can be explained by a variation in the defect content of the ceramic, and can be analysed using the Griffith equation.

It is known that introducing a secondary phase in ceramics may influence the size of the Griffith defects (c_f) by limiting their length. Two cases are therefore possible depending on the distance d between the secondary phase particles [16]: (i) $d > c_f$, the effect of particles on the effective length of the Griffith cracks might be expressed as follows: ($c \propto c_f^2(1 - \phi)$ where ϕ is the volume fraction of particles with a weak dependence of strength on the concentration, i.e. $\sigma \propto (1 - \phi)^{-1/2}$; and (ii) if $d < c_f$, the distance between the particles $d = 4R(1 - \phi)/3\phi$ (where R is the particle radius) directly defines the effective size of the defects, and substitution of d in the Griffith equation gives the dependence of strength of concentration:

$$\sigma = \frac{K_{Ic}}{1.23} \left(\frac{3\phi}{4R(1 - \phi)} \right)^{1/2} \quad (1)$$

The two regions are shown schematically as I and II in Fig. 7.

As revealed by the fracture investigations, the fracture sources connect with defects exhibiting inter-

crystalline behaviour. For this reason, only ZrO_2 particles that are situated along the Al_2O_3 grain boundaries can limit the size of the Griffith defects. The analysis of stress fields in the vicinity of m- and t- ZrO_2 revealed that the particles, of m- ZrO_2 alone can limit the length of flaws which play the role of crack nuclei. The calculation from Equation 1 are in agreement with the experimental values obtained (Fig. 6a) when it is assumed that only 10% of particles exert an influence on the effective dimensions of defects, that is, only 10% of ZrO_2 particles are effective dispersion-strengthening ones. At $R = 1 \mu\text{m}$ and $\phi_{\text{tot}} = 7.3, 15, 23.3$ and 32% we obtained values of $d = 181, 84, 57$ and $42 \mu\text{m}$, respectively.

The corresponding relation $\sigma_f \propto d^{-1/2}$ as shown in Fig. 7 for the concentration range 7.3–23.3 vol % ZrO_2 is in good agreement with the above-mentioned concepts. The tangent of the curve slope angle α allows one directly to define the fracture toughness $K_{Ic} = 1.23 \tan \alpha$, the value of which equal $7.2 \text{ MPa m}^{1/2}$ from the data of Fig. 7. The strength value at 32 vol % ZrO_2 deviates from the linear relationship; this may be conditioned by a spontaneous microcracking phenomenon at ZrO_2 concentrations higher than 32 vol %. Spontaneous microcracking leads to a sharp growth of the defect size with a respective decrease of the strength.

Thus the investigated hot-pressed Al_2O_3 -based ceramics, in spite of their microstructural inhomogeneity and heterophase state (t-, t'- and m- ZrO_2 phases) have a relatively high level of fracture toughening ($\sim 7 \text{ MPa m}^{1/2}$) which does not vary in a wide range of ZrO_2 concentrations.

4. Summary

Thus the investigated hot-pressed Al_2O_3 -based ceramics, in spite of their microstructural inhomogeneity and heterophase state, t-, t'- and m- ZrO_2 phases, have a relatively high level of fracture toughening ($7 \text{ MPa m}^{1/2}$) which does not vary within a wide range of ZrO_2 concentration.

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