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Mechanical Behaviour of Yttria- and Ferric Oxide-Doped Zirconia at Different Temperatures

G. A. Gogotsi

Institute for Problems of Strength, National Academy of Sciences of Ukraine, 2 Timiryazevskaya Str., 252014 Kiev, Ukraine

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Abstract: The variation of strengh, deformability, fracture toughness and other characteristics of partially stabilized zirconia ceramics (Y–Fe–PSZ) doped with 3% yttrium and 3% ferric oxide over a temperature range from −140 to 1400°C were investigated. Fracture toughness (K_{1c}) values obtained by the methods such as SENB, SEPB, IS and IF were compared. Lower temperatures resulted in an increase in fracture toughness by approximately 29%. Using the Vickers indents as stress concentrators for the IS tests we derived the relationship between K_{1c} values and mean values of radial crack length described by a second-degree polynomial. The data for zirconia (Y–PSZ and Mg–PSZ) and silicon-nitride ceramics, as well as the fractographic data, were used to analyse the results. It was established that the addition of ferric oxide exerted a positive effect on the strengh and fracture toughness of zirconia ceramics. © 1998 Elsevier Science Limited and Techna S.r.l.

1 INTRODUCTION

As single crystals transformation-toughened zirconia-based ceramics stabilised with yttria are usually linear elastic and those stabilised with magnia and ceria are usually inelastic at room temperature.[1] This gives rise[2] to other differences in their behaviour on loading. However, the mechanical behaviour was mainly studied on the materials characterised with considerable inelasticity[3–5] while the materials with the limit of proportionality not greatly differing from the ultimate strength were given little attention. Since any possible inelasticity can affect the evaluation of real performance of ceramics, Y–PSZ with the addition of ferric oxide somewhat changing their mechanical behaviour were used for the investigation.

2 MATERIALS AND METHODS

The ceramics under study were produced by slip-cast molding followed by isostatic pressing at 2 kbars and sintering. Besides ZrO_2 of technical purity, they contained 3% Y_2O_2 and 3% F_2O_3 (see Ref. 6 for more detailed information).

To compile additional information for the data analysis, we also studied other materials (Table 1). In particular we tested conventional partially stabilised ceramics Y–PSZ produced almost in the same way as the above,[6] tetragonal polycrystalline ceramics Y–TZP prepared by EMPA (Switzerland), their fracture toughness being tested room temperature (RT),[7] and partially stabilised ceramics Mg–PSZ of TS-grade made by Nilcra Ceramics (Australia), being investigated at low temperatures (LT).[8] We also used Y–PSZ crystals (of the same composition as Y–PSZ–C) prepared by the Institute of General Physics of Russian Academy of Sciences,[9] comparatively uniform reaction-bonded (Si_3N_4–RB[10]) and hot-isostatically-pressed (Si_3N_4–HIP[11]) silicon nitride ceramics.

Rectangular beam specimens were prepared from the blanks and ground with diamond tools, their edges being rounded. To prepare the specimens for flexural fracture toughness tests, three stress

Table 1. Materials for additional tests

Materials	Index	Additives (%)	Brittleness measure, χ	Flexural strength, S (MPa)	Modulus of elasticity, E (GPa)
Y–TZP	TZP	Y_2O_3 (3)	1	774	211
Y–PSZ	PSZ	Y_2O_3 (3)	1	425	197
Y–PSZ–C	C	Y_2O_3 (3)	1	506	297
Mg–PSZ	Mg	MgO (9)	0.46	641	207
Si_3N_4–RB	S-RB	SiC, (30)	1	165	178
Si_3N_4–IP	S-HP	Y_2O_3 (4)	1	658	314

concentrators were applied on to the surface along their axis. Therefore, in these cases the experimental points possess double designation the first part of which is the specimen number and the second one is the index of stress concentrator location. For indentation tests the fragments of these specimens were used. To study the indenter impressions and to observe the crack development, the sides of the specimen were polished with diamond paste.

The investigations were mainly based on our procedures for specimen testing at different temperatures.[12] In accordance with them the displacement of specimens (δ) and the applied loads (P) were measured on 4-point flexure (Fig. 1). For this purpose we used experimental loading modules mounted on conventional test machines. The δ values were measured by LVTD with a sensitivity of $\pm 0.1\,\mu m$, the specimens were cooled under liquid nitrogen vapors. The loading module for RT indentation tests was equipped with the Vickers indenter and the 2-co-ordinate support table.

The inelasticity of ceramics was estimated by their brittleness measure χ^2 which is equal to the ratio of the specific elastic energy accumulated in the material by the moment of its fracture to the total specific energy spent for its deformation by the same moment:

$$\chi = \sigma_u^2/2E \int_0^{\varepsilon_u} \varepsilon \tag{1}$$

where σ_u is the ultimate strength, E is the elasticity modulus, ε_u is the ultimate strain and σ is the stress at current strain values ε. For elastic materials the flexural strengths were calculated by the conventional equation of applied mechanics:[13]

$$S = \frac{3s}{bh^2} P \tag{2}$$

For inelastic materials Nadai's equation[14] was used (for designations see Fig. 1(b):

$$\sigma = \frac{2s}{bh^2}\left(P + \frac{}{2d\delta}\right) \tag{3}$$

The ε values were determined as

$$\varepsilon = \frac{4h}{L^2}\delta \tag{4}$$

To calculate the ultimate strength σ_u and the ultimate strain ε_u, the ultimate values of P and δ were substituted into (3) and (4), respectively.

The fracture toughness results were obtained by several competing procedures (Table 2): by the simplest and widely used method (SENB); by the method which appears to be the most reliable (SEPB), by the method characterised by a simple preparation of stress concentrators (IS); and by the method requiring a small amount of test materials (IF).

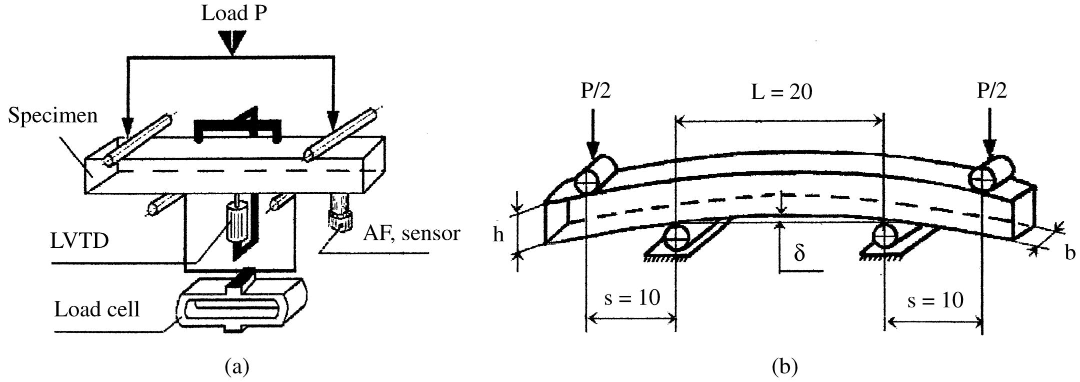
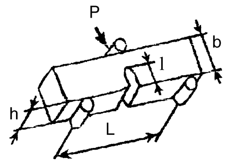
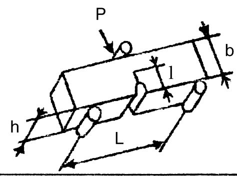
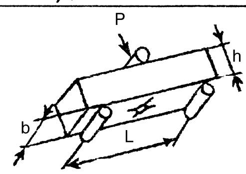
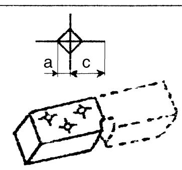


Fig. 1. (a) Ceramtest-type loading module for flexural tests (strength, fracture toughness, deformability, acoustic-emission and elasticity) of ceramics at RT and (b) schematic drawing of a specimen for the strength test.

Table 2. Test methods

Method	Specimen
Single edge notched beam SENB	
Single edge precracked beam SEPB	
Indentation strength IS	
Indentation fracture IF	

SENB and SEPB test results were processed as usual by: [15]

$$K_{1c}^2 = \frac{3LP}{2hb^2} l^{0.5} F(\alpha). \qquad (5)$$

Here

$$a = //b,$$

$$F(\alpha) = \frac{1.99 - \alpha(1-\alpha)(2.15 - 3.93\alpha - 2.7\alpha)}{(1+2\alpha)(1-\alpha)^{1.5}}$$

IS fracture toughness was determined according to [16]

$$K_{1c} = \eta (E/H_V)^{1.8} \left(S_i Q^{1/3}\right)^{3/4} \qquad (6)$$

Here $\eta = 0.59$, H_V is the Vickers hardness, Q is the indentation load, and S_i is the flexural strength of the specimen with the impression.

In the IF method the K_V values (K_V is defined as an approximation of K_{1c} for the IF-method) were determined by:[17]

$$K_{v_1} = 0.036 E^{0.4} Q^{0.6} a^{0.8} c^{-1.5} \qquad (7)$$

But since[17] is designed for the cases of median cracks formed under the Vickers indenter (until now we revealed them in ZrO_2 materials only in cubic single crystals), the equation[18] for the Palmqvist crack was also applied:

$$K_{v_2} = 0.018 H_V (E/H_V)^{0.4} a^{0.5} \left(\frac{c-a}{a}\right)^{0.5} \qquad (8)$$

3 RESULTS

Fe_2O_3-doped ceramics sintered at different temperatures (Table 3) were tested on 3-point flexure

Table 3. Test results for ZrO_2-ceramics with Y_2O_3 and Fe_2O_3

Sintered temperature (°C)	Test temperature (°C)						
		AT		800		1200	
	χ	S (MPa)	K_{1c}(MPa m$^{1/2}$)	S (MPa)	K_{1c}(MPa m$^{1/2}$)	S (MPa)	K_{1c}(MPa m$^{1/2}$)
1320	0.99	812	10.9	308	4.3	—	—
1330	0.94	859	8.8	237	3.5	—	—
1340	0.88	977	13.3	303	5.5	207	2.3
1350	0.95	786	12.0	217	3.3	120	2.9

(40 mm span). It was established that at 1200°C or higher they exhibited considerable creep (crosshead speed was 0.5 mm min^{-1}). Proceeding from the data obtained, ceramics sintered at 1340°C were chosen as optimum ones, they were designated Y–Fe–PSZ ("Fe" is the index for Fig. 2) and investigated at RT and LT. The results of their strength determinations (eqns (2) and (3)) at RT on 4-point flexure (20–40 mm span) are summarised in Table 4. Fracture toughness results (eqns (5) and (6)) on 3-point flexure (20 mm span) are depicted in Fig. 2, the data for other materials are also presented for comparison. The K_v values (eqns (7) and (8)) as a function of the load applied to the indenter are demonstrated in Fig. 3.

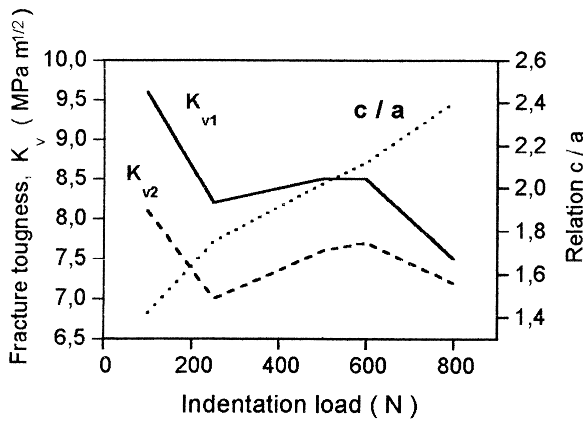


Fig. 3. Fracture toughness and c/a relation for Y–Fe–PSZ on the Vickers indentation.

4 DISCUSSION

Data in Table 4 show that Y–Fe–PSZ displays not only the scatter of strength values which is usually taken into account, but also that of the brittleness measure.

The analysis of Fig. 2 reveals a growth of fracture toughness with a fall of test temperature both for the ceramics under study and for other ceramics and single crystals with Y_2O_3. In this case the S value for Y–Fe–PSZ ceramics increased up to 917 MPa. On the whole these data do not contradict other results of Refs 1, 8, 19. At the same time the fracture toughness of values for Si_3N_4 ceramics (S–HP and S–RB in Fig. 2) remained practically unchanged under such conditions.

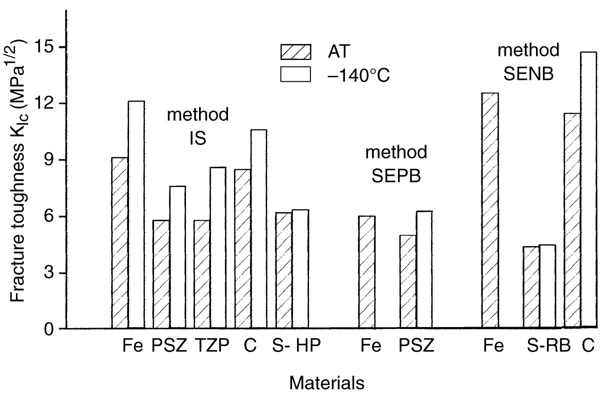


Fig. 2. Results of comparative fracture toughness tests at RT and −140°C.

Inelastic ceramics Mg–PSZ exhibited an increase and then a decrease of their K_{1c}-values (Fig. 4) with lower test temperatures. This effect (see also Ref. 8) was observed in the temperature range of a considerable inelasticity decrease (in Fig. 4 it is shown as a change of the brittleness measure χ) for these ceramics in the zone of their first low temperature elastic–inelastic transition.

During the K_{1c} calculations of values based on SEPB data (eqn (4)) one could pay attention to a considerable dependence (Table 5) of the results on the methods of determining the crack length which were as follows: (i) compliance data for the specimen with a crack; (ii) mean values of crack lengths on both sides of the specimen or (iii) measurements (ASTM E-399[20]) on the fracture surface of the specimen (Fig. 5). If we compare IS and SEPB fracture toughness data (Fig. 2 and Table 5), the result corresponding to the third method appear to be the closest ones. It should be noticed that just this method is recommended, e.g. in Refs 21, 22. Unfortunately, we could hardly overcome (and not always) technical problems associated with measurements on fracture surfaces which also took place in.[21]

The data of Table 5 are also interesting because they, for instance, explain the difference in the shape of R-curves[23] plotted by methods (i) and (ii) and generally point to the significance of such curves obtained by the method (i) on flexure.

A detailed consideration of IS fracture toughness data for Y–Fe–PSZ ceramics (Table 6) can hardly

Table 4. Test results for Y–Fe–PSZ ceramics at RT (4-point flexure)

	35	41	37	45	39	44	40	46	Average	SD
χ	0.7	0.82	0.86	0.92	0.93	0.96	1	1	0.88	0.1
σ_u (MPa)	760	767	673	637	717	791	638	765	711	62
$\varepsilon_u\,10^{-4}$ (m m^{-1})	45.9	42.0	41.1	35.7	38.0	42.9	33.1	40.2	39.9	4.1
S (MPa)	866	811	698	658	732	797	638	765	746	79
E (GPa)	203	196	181	188	196	189	193	190	192	7

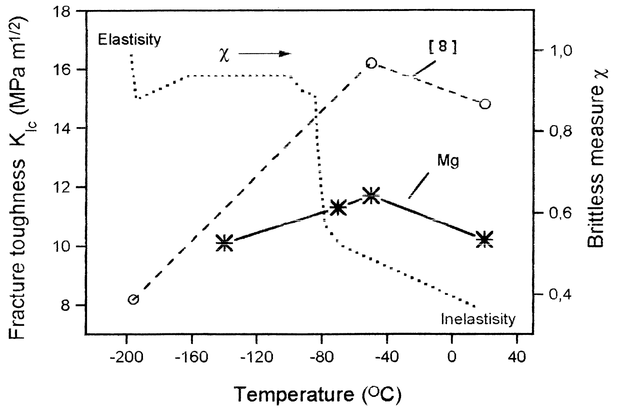


Fig. 4. Fracture toughness variation for Mg–PSZ ceramics in the temperature range of inelastic–elastic transition.

reveal any unambiguous dependence between K_{1c} values and crack lengths c formed on the indentation of the specimen. Taking into account the observation of the authors of this method[16] that a certain change in the length of such cracks did not exert a noticeable influence on the values of K_{1c} and remaining within the Griffith theory, we assumed the following: if in our case the geometric parameters of loading are constant and the distribution of acting stresses in the specimen is the same, the beginning of uncontrolled fracture of every material is determined by its own critical crack length l_{cr}. Thus, an initial crack c of any length should develop up to the l_{cr} value during the flexural loading of the specimen. Therefore, there are no grounds to consider (see in Ref. 21 for observations of different authors on this problem) that such heterogeneous ceramics as Y–Fe–PSZ should display an increase of 2.52 times, as it was shown in Ref. 16 and confirmed in Ref. 24. The fact that every material is characterised by its own behaviour of subcritical crack (c) growth is also confirmed by the differences

Table 5. Effect of crack length measurement procedure on K_{1c} values (SEPB)

(i) Method		(ii) Method		(iii) Method	
l (mm)	K_{1c} (MPa m$^{1/2}$)	l (mm)	K_{1c} (MPa m$^{1/2}$)	l (mm)	K_{1c} (MPa m$^{1/2}$)
Y–Fe–PSZ					
2.31	2.1	2.79	3.2	3.09	4.5
3.01	4.7	3.0	5.0	3.34	7.4
3.24	4.7	3.0	3.2	3.41	6.1
3.52	5.4	—	—	3.71	6.9
Y–PSZ					
2.91	3.8	2.96	4.0	3.17	5.0
—	—	2.77	5.3	2.9	6.6
—	—	2.77	5.3	3.0	5.8
Mg–PSZ					
2.22	9.5	2.33	10.2	2.60	12.0
2.23	9.8	2.51	11.6	2.55	11.9

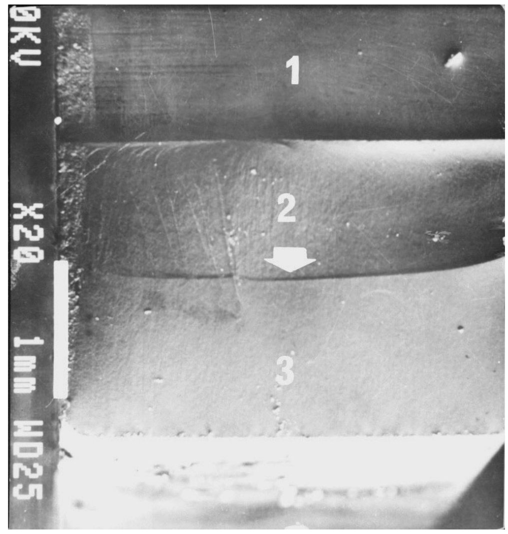


Fig. 5. Fracture surface of the specimen (SEPB method): 1 — saw notch, 2 — precrack front, 3 — fast fracture region.

in prefracture zones on load–displacement curves for the IS specimens (Fig. 6).

Having no possibility to make direct measurements confirming the above, we tried to find a characteristic associated with l_{cr}. As the first approach, we used an averaged crack length near the indenter impressions (c_{av} in Table 6) specific for each specimen. For its determination on each fragment of IS specimens tested at a load of 500 N, 12 impressions were made. The curves were plotted with c_{av} value (Fig. 7); they are described by second-degree polynomial the coefficients of which coincide in rough approximation for RT and −140°C.

As opposed to the above, the results of similar Y–PSZ tests (Table 7) did not reveal any specific features.

Table 6. Test results for Y–Fe–PSZ ceramics (IS method)

Specimen (no./index)	Test temperature (°C)				
	AO		−140		
	K_{1c} (MPa m$^{1/2}$)	c (μm)	K_{1c} (MPa m$^{1/2}$)	c (μm)	c_{av} (μm)
23/1	7.9	338	—	—	
/2	—	—	10.4	337	348
/3	—	—	10.5	339	
24/2	—	—	14.9	262	
/3	11.6	260	—	—	266
25/2	—	—	15.2	278	
/3	—	—	13.7	241	278
64/2	—	—	12.2	295	
/3	8.7	305	—	—	298
66/1	—	—	10.2	334	
/2	8.3	331	—	—	312
/3	—	—	11.3	289	
69/1	8.6	258	—	—	
/2	—	—	11.5	264	297
70/1	9.4	271	—	—	
/2	—	—	12.2	267	283

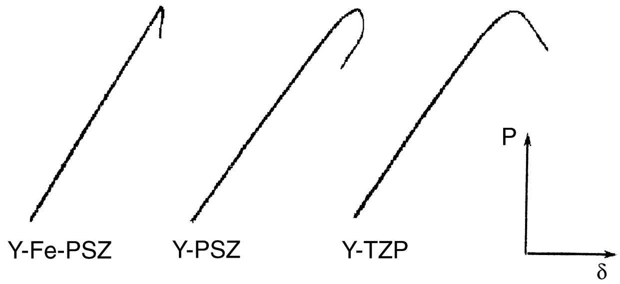


Fig. 6. Final sections of prefracture zones on load–displacement curves for the IS-tested specimens of different ceramics.

The tests by the IS method show that Y–Fe–PSZ ceramics (data were obtained on other series of specimens) exhibit lower K_{1c} values with an increase in indentation loads. Thus at 100, 250 and 500 N loads they were equal to 11.07, 11.1 and 9.95 MPa $m^{1/2}$, respectively. For Y–PSZ the picture is approximately the same, their K_{1c} values were 6.1, 5.8 and 5.8 MPa $m^{1/2}$, respectively.

Considering these unusual results, we tried to verify the reliability of the test method used. For this purpose Y–TZP ceramics and the test data of Ref. 7 were employed. A certain agreement between our data and the data by other authors was established (Table 8).

The analysis of IF data (Fig. 3) has demonstrated that higher indentation loads result in lower

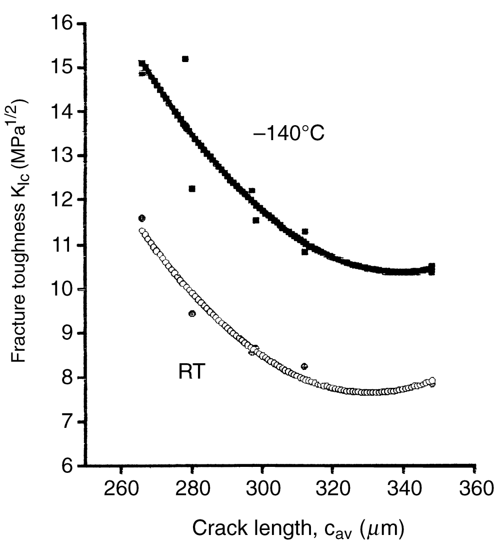


Fig. 7. K_{1c} values for Y–Fe–PSZ ceramics as a function of average crack lengths near the indenter impression (IS method).

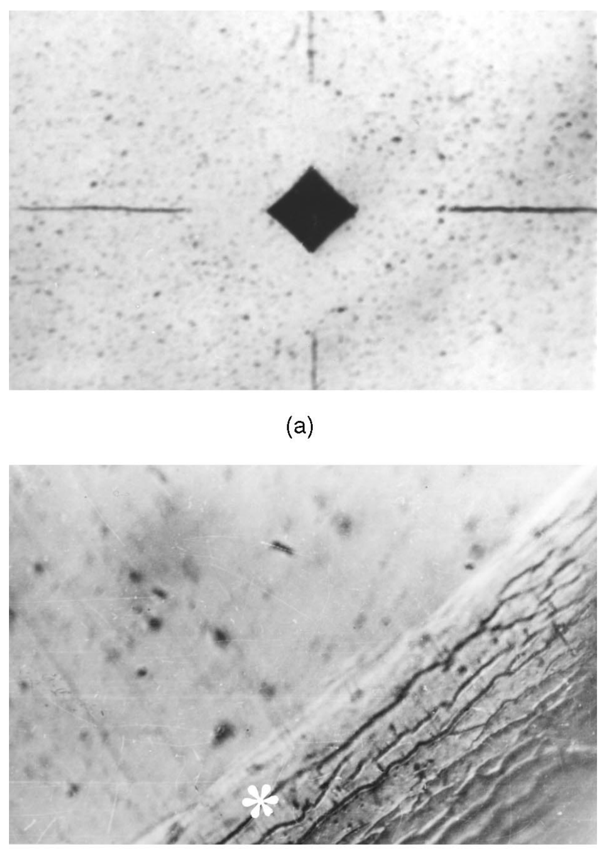
Table 7. Test results for Y–PSZ ceramic (IS method)

Specimens (no./index)	8/3	6/3	3/3	7/3	5/3	13/3
K_{1c} (MPa $m^{1/2}$)	5.95	5.95	5.81	5.77	5.75	5.62
c (μm)	4.00	4.11	4.35	4.24	4.17	4.28
c_{av} (μm)	4.10	4.12	4.35	4.11	4.08	4.24

K_v values. They also differ considerably depending on the equation applied for calculations. It is typical that in all the cases of indentation only Palmqvist cracks were formed in the specimens (Fig. 8(a)). For Y–Fe–PSZ ceramics the ratio of c/a achieved 2.3 (usual condition of validity of applying eqn (7) at loads close to those inducing the failure of indenter impressions (Fig. 8(b)). It is interesting that similar failure of indenter impressions was earlier observed also in the tests of ZrO_2 PSZ crystals.[19] It appears, e.g. that the ceramics under study do not meet the requirements set forth in Ref. 22, only when they meet them, their fracture toughness can

Table 8. Fracture toughness results for Y–TZP ceramics

Test method	IS			Chevron notched beam method
No. of specimens	4	3	4	4
K_{1c} (MPa $m^{1/2}$)	5.67	5.82	5.61	5
SD (MPa $m^{1/2}$)	0.38	0.1	0.09	0.27
Indentation load (Q)	100	500	—	—
Investigators	IPP	IPP	EMPA[7]	ESN[7]



(a)

(b)

Fig. 8. Indentation results for Y–Fe–PSZ specimens: (a) radial crack pattern near the impression (surface layer is ground-off) at 500 N; (b) fracture zone of the impression at 800 N (* surface of impression).

reliably be evaluated by the IF method. It should be noted that the use of eqn (8) does not introduce any specific features in the unambiguity of data obtained by different test methods.

5 CONCLUSIONS

We investigated the variation of strength, deformability, fracture toughness and other characteristics of partially stabilised zirconia ceramics (Y–Fe–PSZ) doped with 3% yttrium and 3% ferric oxide over a temperature range from −140 to 1400°C. Fracture toughened (K_{1c}) values obtained by such methods as SENB, SEPB, IS and IF were compared. Lower temperatures resulted in an increase in fracture toughness by 29% approximately. For the IS test the Vickers indents used as stress concentrators we derived the relationship between K_{1c} values and mean value of radial cracks length described by a second-degree polynomial. It was demonstrated that for the SEPB-method K_{1c} values were strongly dependent on a procedure of measuring the crack initial length. The data for zirconia (Y–PSZ and Mg–PSZ) and silicone–nitride ceramics as well as fractographic ones were used to analyse the results.

It was established that the addition of ferric oxide exerted a positive effect on the strength and fracture toughness of Y–Fe–PSZ ceramics. This is associated with a decrease of brittleness caused by their relative inelastisity.

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