# **Strength and Fracture Toughness of Zirconia Crystals**

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## *Abstract*

*Single crystals up to 40 mm wide and 120 mm long made o[zirconia with yttria addition were investigated over the temperature range of*  $-140$  *to*  $1400^{\circ}$ *C by the methods conventionally used for advanced ceramics. The stress-strain curves were analysed. Up to 1000°C the curves of all the crystals were linear (the*  'brittleness measure',  $\chi = 1$ ), and on heating up to  $1400^{\circ}$ C a minimum value of the 'brittleness measure' *for partially stabilized crystals was 0.73. At 1400* $^{\circ}$ *C the MOR of cubic single crystals is almost 2 times higher than at*  $20^{\circ}$ *C and is greatly dependent on a loading rate. The strength of PSZ single crystals decreases with an increase in temperature. The decrease of test temperature from ambient to*  $-140^{\circ}$ *C results in a 20% increase in strength of these crystals, the latter being practically independent of a loading rate. The relation between the elastic moduli and the .fracture toughness of single crystals was investigated. A maximum value of*  $K_{Ic} = 16 MPa$  *m*<sup> $1/2$ </sup> *at Ea = 301 GPa was measured. It is shown that the Rcurves are flat and that a fracture barrier effect exists. The mechanical behaviour of crystals was also studied by Vickers indentation. Partial substitution of yttria with ytterbia increases the fracture toughness of these materials. The results of fractographic investigations were used to analyse the test data. Information sufficient to compare single crystal materials with advanced ceramics and necessary to estimate their potential applications in ambient- and hightemperature devices has been obtained.* 

*Einkristalle mit einer Dicke bis zu 40 mm und einer* Länge bis zu 120 mm aus Zirkoniumdioxid mit Yttriumoxid-Zusätzen wurden im Temperatur*hereich von -140 bis 1400<sup>°</sup>C mittels der üblichen* Methoden für moderne keramische Werkstoffe untersucht. Ihre Spannungs-Dehnungs-Kennlinien wurden *untersucht. Bis IO00°C weisen die Kennlinien aller Kristalle einen linearen Verlauf auf ('das Spr6dig* $k$ eitsma $\beta$ ',  $\gamma = 1$ ). Beim Aufheizen auf Temperaturen bis 1400°C betrug der geringste Wert des 'Sprödig*keitsmafles' teilweise stabilisierter Kristalle 0"73. Bei 1400°C ist der MOR kubischer Kristalle fast doppelt*  so *hoch wie der bei 20°C und ist stark yon der Belastungsgeschwindigkeit abhiingig. Die Festigkeit yon PSZ-Einkristallen nimmt mit zunehmender Temperatur ab. Die Senkung der Temperatur yon*   $Raum temperature \, auf -140^{\circ}C \, führt \, zu \, einer \, Festig$ *keitssteigerung dieser Kristalle urn 20%, wobei die*  Festigkeit hier nahezu unabhängig von der Bela*stungsgeschwindigkeit ist. Es wurde der Zusammenhang zwischen dem Elastizitiitsmodul und der Bruchziihigkeit der Einkristalle untersucht. Als Maximalwert wurde*  $K_{Ic} = 16 MPa \sqrt{m}$  *bei*  $E_a = 301 GPa$ *gemessen.* Es *wird gezeigt, daft die R-Kurven flach verlaujen und daft ein Bruchbarrieren-Effekt vorliegt.*  Das mechanische Verhalten der Kristalle wurden au- $\beta$ erdem mittels Vickers-Härtemssungen studiert.

*Le comportement de monocristaux de zircone contenant de l'oxyde d'yttrium d'une taille maximale de*  40 mm de large et de 120 mm de long, a été examiné dans une gamme de température comprise entre moins

*140 et 1400°C, en utilisant les techniques habituellement employées pour caractériser des céramiques de* pointe. Les courbes contrainte-élongation ont été *analysées. Jusqu'à 1000°C, toutes les courbes relevées* sont linéaires (c'est à dire un 'facteur de fragilité',  $\chi = 1$ ), tandis qu'à la température maximale testée, *c'est gt dire 1400°C, une valeur minimale du 'facteur de fragilité' est constatée:*  $\gamma = 0.73$ . *A 1400°C, le module de rupture des monocristaux cubiques est presque 2 fois plus élevé qu'à 20°C et il est très dépendant de la vitesse de mise en charge. La résistance mécanique des monocristaux de PSZ diminue quand la température* augmente. De même, lorsque l'on examine la ré*sistance en dessous de la tempirature ambiante et ce*   $jusque -140°C$ , une augmentation de 20% est *mesurée, apparemment sans dépendance de la vitesse de raise en charge. La relation entre les modules élastique et la ténacité à la rupture a été également* étudiée pour les mêmes monocristaux. Leur comporte*ment mécanique a aussi été évalué par indentation Vickers. Une valeur maximale du*  $K_{Ic}$  *de 16 mPa*  $\sqrt{m}$ *correspond à*  $R_d = 301$  *GPa. Les auteurs montrent igalement que les courbes R sont plates et qu'un effet*  de barrière à la rupture existe. La substitution partielle de l'yttrium par l'ytterbium améliore la *ténacité de ces matériaux. Enfin, les résultats sont également interprétés grâce à l'examen des faciès: de rupture. Une somme de renseignements permettant la comparaison des monocristaux et des céramiques de pointe analogues a été obtenue; elle permet d'estimer valablement leur applicabilité en tant que composants travaillant à température ambiante et à haute*  $temperature$ .

#### **1 Introduction**

The investigations of single crystals are often performed to get information which is useful for understanding the behaviour of polycrystalline partially stabilized zirconia (PSZ) and tetragonal zirconia polycrystals (TZP), since the influence of grain boundaries, their random orientation and other effects can be excluded. But the technology of fabricating PSZ single crystals (PSZ-SC) based on direct high-frequency skull-melting is also of great interest. It is distinguished by the use of raw materials of any size distribution (i.e. they are cheaper than those which are required for producing advanced zirconia ceramics), high efficiency, comparatively low energy intensity, waste-free operation (i.e. remelting of machining wastes, failed components), etc. For fabricating and studying PSZ-SC, one can take advantage of experience gained in the use of cubic zirconia single crystals (CZ-SC) which have found application in optics, laser engineering, the jewellery industry and in other fields. For

example, in the USSR the large-scale production of such jewellery materials (fianite) is established. $<sup>1</sup>$ </sup>

Investigating PSZ-SC and CZ-SC researchers studied strength and fracture toughness as a function of temperature,<sup>2,3</sup> plasticity and creep,<sup>4,5</sup> and other properties. Attention was paid to the problems of elastic anisotropy<sup> $6,7$ </sup> and to the behaviour of crystals on indentation.<sup>3,8</sup> Many investigations were performed to elucidate the mechanisms determining the nature of resistance to failure and deformation. $9,10$  Thus, voluminous and rather important information on these materials was accumulated.<sup>11</sup>

The data presented in these and other publications allow it to be concluded that zirconia single crystals can have use not only for jewellery applications but also for fabricating the cutting tools used in medicine (Fig. 1) and in the machining of metals and nonmetals; dies for the textile and cable industries, components of high-temperature bearings for various thermal devices and others.

Unfortunately, the difficulties arise during the practical use of existing information, since in many cases the most valuable data were obtained on miniature specimens suitable only for physical experiments. For example, bending tests were performed on  $2 \times 3$  mm specimens at a span of  $12 \text{ mm};^{2,3}$   $2.5 \times 2.5 \times 6.0 \text{ mm}$  prisms were compressed<sup>10</sup> and so on. It should also be noted that many publications discuss the properties of crystals produced by the same company. But any publications on the crystals developed in the USSR, where quite innovatory investigations in this field have been performed under the guidance of V. M. Prokhorov, the Noble prize winner, are practically nonexistent. The present work is a further development of the above investigations.

Appreciating the potential of these materials, they have been studied using the same approach as that used for other advanced ceramics. The data were probably first analysed from the engineering point of view, i.e. as is done for ceramic materials, but not



Fig. 1. PSZ crystal eye's knife.

from the point of view of physics, as is usually performed in papers devoted to single crystals.

#### **2 Materials and Methods**

Crystals stabilized with  $3 \text{ mol}$ %  $Y_2O_3$  (SC-1) and with  $1.5 \text{ mol\%}$  Y<sub>2</sub>O<sub>3</sub> + 1.5mol<sup>%</sup> Yb<sub>2</sub>O<sub>3</sub> (SC-2) produced at the Verkhnedneprovsk Mining and Steel Complex<sup>12</sup> and crystals stabilized with  $3 \text{ mol\%}$  $Y_2O_3$  (SC-3) produced at the Institute of General Physics, Russian Academy of Sciences<sup>13</sup> were chosen for the investigations. For additional investigations, CZ-SC containing 10, 12, 14, 15, 16, 20 and  $35 \text{ mol}$ % Y<sub>2</sub>O<sub>3</sub> and produced on the same equipment as SC-3 were used. All the crystals were obtained by the direct high-frequency skull-melting technique. 6 (The equipment used in the present work for fabricating single crystals was produced under the guidance of the same authors.) The design of a water-cooled skull assembly (flat bottom, without narrowing or seed) did not limit the number of crystals growing in one melting, and a sintered shell provided multicentre nucleation.

The crystalline blocks of SC-1 and SC-2 were  $10-30$  mm wide and  $40-70$  mm long (about the same as in Refs 2 and 3) and those of SC-3 were up to  $40 \text{ mm}$  and  $120 \text{ mm}$ , respectively (Fig. 2). Their amount reached 30 kg in one crystallization process.

Zirconia powders (99-0% purity), as well as yttria powders of a 99.9% purity for SC-1 and SC-2 and of a 99.99% purity for SC-3, and  $YbO<sub>2</sub>$  powders (99-9% purity) were used for batch preparation.

Specimens  $(3.5 \times 5 \times 50 \text{ mm})$  were cut from the crystalline blocks approximately in the direction of



Fig. 2. Single crystals: 1, PSZ-SC  $(3 \text{ mol\% Y}, O_3)$ ; 2, CZ-SC  $(10 \text{ mol\% Y}_2\text{O}_3)$ .

their growth but in such a way that in each case a maximum number of these specimens could be prepared. Any special sampling, except for the visual control of cracks in the specimens, was not performed. It is characteristic that in Ref. 2 the absence of strict orientation of the specimen surfaces under tension relative to the crystallographic directions is also noted, leading, in the authors' opinion, to the variation of results.

The surfaces of specimens were ground along their axes, and their edges were rounded off.

The authors used the test methods of their system of certification<sup>14</sup> for advanced ceramics already evaluated on different materials,<sup>15</sup> including  $PSZ$ and TZP. 16

Ceramtest-type devices developed at the Institute for Problems of Strength were used for specimen loading. They are installed on standard testing machines and provide high-accuracy determina-





Fig. 3, Fractured surfaces of specimens after the determination of R-curves: (a) SC-3a magnification  $\times$  10; (b) SC-3b magnification  $\times 60$ ; 1 and 2, successive notches of a specimen; 3, initial sharp crack formed under rigid loading conditions of a specimen on its cross compression; 4, fracture area formed on the propagation of a crack.

tions of specimen displacements as a function of an applied load. The displacement was monitored by a precision LVDT with a resolution of  $\sim 0.1$  um. Bending tests were performed at spans of 20/40 mm for four-point bending and of 20 or 40 mm for threepoint bending which corresponds to the standards of different countries.<sup>17</sup> For fracture toughness determinations, the halves of bars  $(1/2 \text{ main length} =$ 25 mm) were used, being notched to a half of their height with a 0.15 mm diamond disc. For strength tests, the bar was installed on loading rolls with its 5 mm side, for fracture toughness tests this side was  $3.5$  mm. Critical stress intensity factors  $(K<sub>L</sub>)$  were calculated according to Ref. 18; R-curves were determined under cyclic loading of specimens with a sharp crack (Fig. 3) in a hard-loading device. Vickers indentation tests were performed in the same device. In this case  $K_{1c}^V$  values were determined according to Ref. 19. Dynamic elastic moduli  $(E_d)$  were calculated from the data of longitudinal ultrasonic velocity measurements in the specimens; static elastic moduli  $(E<sub>st</sub>)$  were determined from displacement-load curves, the level of an applied load being 0-05-0.15 of the ultimate one. The strength was calculated by the classical Nadai equation. The brittleness measure,  $1<sup>5</sup>$  $\chi$ , an energy characteristic of the deviation of the stress-strain curves from linearity, was calculated from the data of four-point bending tests.

### **3 Results and Discussion**

For SC-1 dynamic elastic moduli were in the range of 147 to 346GPa (average value is 230GPa at a standard deviation of  $\pm$  48 GPa for 88 specimens). For other specimen lots of this material the picture was about the same.<sup>12</sup> For SC-2 these values varied within 168 and 319 GPa (average value is 211 GPa at a standard deviation of  $\pm 46$  GPa). For SC-3 specimens the scatter in elastic moduli appeared to be smaller, but they were grouped about two values

(Table 1) which caused the division of this material into SC-3a and SC-3b. It should be noted that in Refs 20 and 21 zirconia single crystals with a different degree of stabilization exhibited longitudinal ultrasonic velocities which were generally higher than the present measurements. However, the relations between dynamic and static elastic moduli (e.g. Table 2) obtained by engineering methods in this investigation and corresponding to standard measurements for ceramics are a strong support of the reliability of these results. In Ref. 7 elastic anisotropy studies on similar CZ-SC exhibited elastic moduli of an order of 360GPa for the crystallographic direction  $\langle 100 \rangle$  and of an order of 170 GPa for the direction  $\langle 111 \rangle$ . It is similar to the observed variations of such values both in PSZ-SC and CZ-SC. Laue X-ray diffraction patterns demonstrated that the axes of SC-3a specimens and of SC-1 and SC-2 specimens with  $E_d \approx 200$  GPa were approximately oriented in the crystallographic direction  $\langle 111 \rangle$  (the same was also observed for CZ-SC); for SC-3b specimens and high-modulus specimens of other materials, the direction was close to  $\langle 001 \rangle$ , which also does not contradict Ref. 7.

Taking into account rather large scatter in data for SC-1 and SC-2 (quite often only 2 or 3 specimens could be cut from some crystalline blocks of these materials), MOR-temperature curves (Fig. 4) were plotted from the data of three-point bending tests at a span of 20 mm. The specimens with elastic moduli close to 200GPa were chosen to provide results comparable with those of Ref. 2.

For the rest of the specimens with elastic moduli of an order of 350 GPa, the ultimate MOR values were 1335MPa for SC-1 and 1668MPa for SC-2. The picture was approximately the same for other similar materials.<sup>12</sup> It should be noted that maximum strength values were measured only for the specimens with high elastic moduli; at the same time such specimens exhibited a comparatively low strength. In the tests with a 40mm span, MOR

<i>Material</i>	Density $(g/cm^3)$	<i><b>Ultrasonic</b></i> velocity (m/s)		Elastic modulus (GPa)	Bending strength (MPa)	Critical stress- intensity	
			Dynamic	<i>Static</i>	Three-point	Four-point	factor, K <sub>Ic</sub> $(MPa \; m^{1/2})$
$SC-3a$ $SC-3b$	$6.04 + 0.01$ $6.03 + 0.01$	$5357 + 83$ $7058 + 122$	$173 + 5$ $301 + 11$	$149 + 6$ $297 + 18$	$862 + 100$ $738 + 91$	$642 + 55$ $506 + 169$	$10.0 + 2.0$ $13.4 + 1.7$

Table 1. Physico-mechanical characteristics of SC-3 at ambient temperature

 $+$  = Standard deviation.

Table 2. Comparison of elastic moduli for SC-3a at ambient temperature (20 specimens)

Dynamic (GPa)		172 181 179 172 173 181 174 172 174 185 173 175 180 179 176 174 177 174 171 172									
Static (GPa)		162 161 162 145 149 150 146 148 147 155 150 145 155 149 145 145 149 146 147 154									



Fig. 4. MOR and  $K_{Ic}$  variations as a function of temperature for SC-1 ( $\bullet$ ) and SC-2 ( $\Box$ ).

values were much lower than in the case of a 20 mm span when the fragments of the same specimens were tested. This phenomenon can be caused by the defects of growth, including certain rotations of the axes of growth during crystallization. Typical fracture origins for SC-1 are shown in Fig. 5. These data question the extent to which even the best results obtained for small specimens can be used for engineering comparisons between single crystals and other advanced ceramics. The above data enable it to be concluded that in a large water-cooled skull assembly multiple centres of crystallization are formed and comparatively small crystals are grown. As the properties of these crystals can differ considerably, therefore, they can only relatively be considered the same material.

The strength tests of SC-3 were mainly performed at a 40 mm span (Tables 1 and 3, Fig. 6). At ambient temperature the stress-strain curves of these crystals as well as of polycrystalline  $Y_2O_3$ -stabilized zirconia ceramics<sup>16,22</sup> are linear. On heating above  $1000^{\circ}$ C the crystals of SC-3a exhibit nonlinearity. In the case of SC-3b, which was of lower strength, only a few specimens were inelastic at 1400°C (Table 3). The rest of them, as well as SC-1 and SC-2 specimens, were elastic until fracture occurred. SC-3b specimens were also investigated at varying travel velocities  $(V<sub>tr</sub>)$  of the cross-arm of the testing machine (this velocity was usually  $0.5 \text{ mm/min}$ ). At 1400°C they exhibited certain sensitivity to a loading rate (though without a considerable change of strength). Thus, when  $V_{tr}$  was 0.05 mm/min, the brittleness measure became 0.67; at  $V_{tr} = 5$  mm/min, its value in all cases was equal to unity, i.e. the crystals were elastic until the moment of fracture.

To present a more exhaustive picture of the mechanical behaviour of the crystals and to compare the results with others, $2.3$  all CZ-SC were



Fig. 5. SC-1 surfaces fractured at: a,  $MOR = 626 MPa$ ; b,  $MOR = 754 MPa$ ; c,  $MOR = 451 MPa$ ; d,  $MOR = 1247 MPa$ .

investigated. It was established that at ambient temperature their strength was slightly different within the scatter of the data  $(MOR \sim 150-$ 210 MPa) at  $E_d = 166 - 295$  GPa.

These data show that the concentration of yttria

Temperature $(^{\circ}C)$		$SC-3a$			$SC-3b$						
	<b>Strength</b> (MPa)	<b>Ultimate</b> strain $(x 10^{-4} m/m)$	<b>Static</b> elastic modulus $(GPa)^a$	<b>Brittleness</b> measure	Strength (MPa)	<b>Ultimate</b> strain $(\times 10^{-4} \; m/m)$	<b>Static</b> elastic modulus $(GPa)^a$	<b>Brittleness</b> measure			
$-140$	802	45.1	176								
20	667	43.3	155		558	18.7	302				
800	450	$28-4$	158								
1000	496	36.8	153	0.85	186	8.2	281				
1400	391	39-1	118	0.73	257	14.9	226	0.91			

Table 3. Four-point bending tests for SC-3

<sup>a</sup> For a group of specimens tested at a given temperature.

in CZ-SC does not exert a noticeable influence on strength (in any case in the range of its content under consideration).

The tests of CZ-SC (10 mol%  $Y_2O_3$ ) at 1400°C and at different  $V_{tr}$  demonstrated (Fig. 7) that the curves may be nonlinear or linear. At 0.05 mm/min the authors failed to fracture the specimen, as was the case in Ref. 2. If PSZ-SC and CZ-SC are compared, the latter are more sensitive to  $V_{tr}$ . Here, in all the cases, the strength of crystals increased with temperature, and the lower the  $V_{tr}$ , the greater this effect.<sup>23</sup>

For single crystals which are conventionally considered to be brittle materials, fracture toughness is of special interest for the evaluation of their possible practical applications. Despite numerous investigations of advanced ceramics, there is no common method which could allow the data on this characteristic to be obtained sufficient to estimate their resistance to failure under any loading conditions. Therefore, in the case of ceramics the

1000 - 800 **- /-140"C**  / /20"C **600-** 800 °  $\sigma$  (MPa) 1000 °C 400°C 400 200  $\sqrt{1 - \frac{1}{2} - \frac{1}{2}$ 0 20 40 60 **E** (10-4 m/m)

Fig. 6. Typical stress-strain curves for SC-3 (test temperatures are given near the corresponding curves):  $\sigma$ , stresses calculated with the account of nonlinearity of a load-displacement curve; e, strain.

authors usually proceed from complex information including both  $K_{Ic}$  measurements on notched specimens and on specimens with a sharp crack as well as on the indentation of the same specimens.

Bending data for notched bars from SC-1 and SC-2 (Fig. 4) were similar to those summarized in Ref. 3. It should be noted that here (as in the MOR determinations) the specimens with  $E<sub>d</sub> \approx 200 \text{ GPa}$ were used. At ambient temperature average  $K_{\text{lc}}$ values were 7 MPa m<sup>1/2</sup> for SC-2 and 10.6 MPa m<sup>1/2</sup> for SC-1. Under the same conditions  $K_{lc}$  values for SC-3 are as follows: 8.0; 8.4; 8.6; 10.2; 12.3; 12.6 (for SC-3a) and 11.3; 13.1; 13.2; 13.3; 16.0 (for SC-3b).

It should be noted that average  $K_{\text{Ic}}$  values (see also Table 1) for SC-1 and SC-3a are quite close. However, they all are higher than the values presented in Refs 2 and 24 for stronger crystals. A similar dependence for  $ZrO<sub>2</sub>$ -based polycrystalline ceramics was also found by Swain & Rose.<sup>25</sup>

The determination of R-curves for those materials questioned the view of their fracture toughness to some extent; for SC-2 and SC-3b they were practically identical (Figs 8(b) and 8(c)), although for SC-2 the value of  $K_{IR} \approx 7 \text{ MPa m}^{1/2}$  was also obtained.<sup> $12$ </sup> It should be noted that for the qualitative evaluation of material uniformity in terms of



Fig. 7. Stress-strain curves for CZ-SC (10 mol%  $Y_2O_3$ ): 1,  $V_{\text{tr}} = 0.5$  mm/min,  $T = 1400^{\circ}$ C; 2,  $V_{\text{tr}} = 5$  mm/min,  $T = 1400^{\circ}$ C; 3,  $V_{tr} = 0.5$  mm/min,  $T = 20$ °C, P, load;  $\delta$ , displacement.



Fig. 8. R-Curves for PSZ-SC at ambient temperature:  $K_{IR}$ , stress intensity factor;  $l_{cr}$ , crack length ( $E_d$ , GPa, are shown near the lines); (a) SC-1; (b) SC-3; (c) SC-2.

resistance to crack propagation, the R-curves were determined for specimens 50 mm long, then for their halves (the latter are shown with a dashed line in Fig.  $8(b)$ ). It is seen that the position of the R-curves for the same material is clearly dependent on the elastic moduli (probably on crystallographic orientation). The *R*-curves for SC-1 (Fig. 8(a)) and SC-3a (Fig. 8(b)) were approximately identical when their  $E_d$ values were about the same. If the data of Fig.  $8(K_{IR})$ values close to those obtained during special  $K_{1c}$ measurements on bars with a sharp crack) are compared with the  $K_{\text{lc}}$  data obtained on notched

latter. For example,  $K_{IR}$  is only 2-3.5 MPa m<sup>1/2</sup> for SC-3a and  $4-6.2$  MPa  $m^{1/2}$  for SC-3b. So it could be concluded that all these materials, as well as yttriastabilized polycrystalline ceramics,<sup>22</sup> exhibit a noticeable fracture-barrier effect:<sup>26</sup>  $K_{1c}$  values obtained on notched specimens exceed those obtained on specimens with a sharp crack.<sup>16</sup>

The CZ-SC materials of all compositions exhibited approximately the same fracture toughness  $(K_{\text{Ic}} = 1.6-2.0 \text{ MPa m}^{1/2})$ , and it does not differ from the value obtained earlier for crystals containing 20%  $Y_2O_3$ .<sup>3</sup> The values of  $K_{1c}$  obtained during the tests of specimens with a sharp crack and the Rcurves for these materials (Fig. 9) were approximately of the same level. For these materials a fracture-barrier effect was also revealed. However, additional investigations are required.

The indentation studies on fracture toughness of ceramics become a matter of certain difficulty in terms of choosing the equations to calculate  $K_{1c}^{27}$ and of determining the parameters<sup>28</sup> necessary for these calculations, in particular for single crystals. Therefore, until standard test methods are adopted, the obtained data can be regarded only as comparative but nevertheless quite interesting from the point of view of estimating the resistance of material surfaces to failure. Polycrystalline zirconia ceramics are considered to form Palmqvist cracks at average loading levels (median cracks at high loading levels are also possible). It was observed that PSZ-SC did not always behave this way (Fig. 10), since fractures along the weakest planes are possible.<sup>29</sup> Also it was not always possible to get indentations in which cracks would propagate from each corner. However, attempts were made to estimate  $K_{1c}^V$  values to make the picture more complete. The authors also performed calculations by the equation for the case of a median crack.<sup>30</sup> The following  $K_{1c}^{V}$  values were obtained for SC-3 materials (the upper number was calculated by the equation of Ref. 19 and the lower number corresponds to the calculations of Ref. 30):



These data demonstrate that crystals with higher elastic moduli (SC-3b) also possess higher fracture toughness.

The Vickers indentation did not reveal any noticeable anisotropy, when one of the diagonals of the indentor coincided with the specimen axis.

In the case of Knoop indentations the conclusions could be quite different, since radial and lateral cracks (Fig. 11) differed qualitatively, depending on



Fig. 9. R-Curves for CZ-SC at ambient temperature (mol%)  $Y_2O_3$  are shown near the lines).

the orientation of the indentor,  $28$  especially for SC-1 crystals.

The comparison between the present results and the results of other authors who investigated PSZ-SC with 3 mol%  $Y_2O_3$  is of additional interest. The present authors could not fracture any crystalline plane at 5 and 10N loads as used in Ref. 21. However, a 50 N load resulted in cracks  $20-30 \mu m$ long for SC-3b (such cracks for 10 N loads are shown in Fig.  $2(a)^{21}$ , the same load on SC-3a gave  $40-70 \mu m$  cracks (they were approximately equal to those shown in Fig.  $3^{21}$ ). The present authors consider that comparative evaluations of fracture toughness of single crystals should be based rather on crack length values at a preset indentation load than on  $K<sub>lc</sub>$  values taking into account the present state of its measurements.

All the CS-ZC compositions did not considerably differ in their fracture toughness under test conditions; the obtained data were in the range of 1.5-2.2 MPa  $m^{1/2}$ , i.e. they were just the same as those obtained by the authors of Refs 3, 28 and 29 for CS-ZC containing about 10 mol%  $Y_2O_3$ .

It is noted that measurements of  $K_{1c}^V$  on CS-ZC with excellent optical properties demonstrated that irrespective of the crystallographic direction, their values across the plane from side to side could vary by up to 30-40%, i.e. the optical uniformity of crystals is not indicative of their 'mechanical' uniformity.

At a load of  $0.5-10$  N the hardness of these CS-ZC compositions was within 14-16GPa (at the same load the values for SC-3 were 14–15 GPa).

#### **4 Conclusions**

The studies on SC-1 and SC-2 have demonstrated that partial substitution of yttria with ytterbia within the same crystal growth technology contributes to their strength and fracture toughness.

The investigations of comparatively large crystals confirmed that in terms of strength they (SC-3b)



Fig. 10. Vickers impressions on the surfaces of a specimen (a) SC-3a at 300N; (b) SC-3b at 100N: 1, impression area after indentation; 2 and 3, the same area after the 1st and 2nd polishings of the specimen surface, respectively.

(b)





(b)

**Fig.** 11. Knoop indentations on the surface of an SC-I specimen: a long diagonal of the impression is (a) along the axis of the specimen ( $\times$  150) and (b) across the axis of the specimen  $(x 130)$ , respectively.

were on a par with similar crystals investigated earlier and in fact were superior to them in  $K_{1c}$  levels.

It is shown that crystals are characterized by flat R-curves and a barrier effect: higher fracture toughness values measured on notched specimens as compared to those of the specimens with a sharp crack.

Having in mind practical applications of PSZ-SC and proceeding from the values of their mechanical characteristics obtained by the test methods used for advanced ceramics, it is interesting to compare them with similar polycrystalline materials.

According to Ref. 11, average values of characteristics for advanced zirconia ceramics are as follows:



Similar measurements for Y-PSZ  $(MOR = 600 -$ 800 MPa,  $K_{1c}=6-8$  MPa  $m^{1/2}$ ) were made elsewhere.<sup>31</sup> The data<sup>16</sup> obtained together with one of the authors<sup>11</sup> for Mg-PSZ display the following MOR values: 526 MPa at 20°C, 180 MPa at 100°C, 40MPa at 1400°C (similar high-temperature strength degradation of Y-TZP<sup>16</sup> and Y-PSZ<sup>22</sup> was

also noted). Notched and sharp-crack Mg-PSZ specimens<sup>16</sup> exhibited  $K_{\text{lc}}$  values of 12 MPa m<sup>1/2</sup>, the values for Y-PSZ were  $9.3 \text{ MPa}$  m<sup>1/2</sup> and 4.8 MPa m<sup>1/2</sup>, respectively.<sup>16</sup> Similar values ( $K_{\text{lc}}$  = 4.1 MPa *m 1/2* for Y-PSZ) were obtained on specimens with a sharp crack elsewhere.<sup>32</sup>

If these data are compared with those summarized in Tables 1 and 3 for SC-3b crystals, an unambiguous conclusion can be reached that their characteristics are not only on a par with Y-PSZ but also in some cases are superior to them (their advantages as compared to other ceramics are well known). Taking into account the advantages of technology, one may say that the studied crystals can be competitive as a structural material for several applications.

Since the investigations on the mechanisms of deformation and fracture of PSZ-SC have not yet been finished, the authors consider it expedient to support the explanation of this problem presented in Refs 3, 9 and 11.

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#### **References**

- 1. Osiko, V. V., Lomonova, E. E. & Bozik, M. A., Crucible-free method of growing oxide crystals from the melt. *Ann. Rev. Mater. Sci.*, 17 (1987) 101-2.
- 2. Ingel, R., Lewis, D., Bender, B. A. & Rice, R. W., Temperature dependence of strength and fracture toughness of ZrO<sub>2</sub> single crystals. *J. Amer. Ceram. Soc.*, **65** (1982)  $150 - 2.$
- 3. lngel, R., Lewis, D., Bender, B. A. & Rice, R. W., Physical, microstructural and thermomechanical properties of  $ZrO<sub>2</sub>$ single crystals. *J. Amer. Ceram. Soc.,* 26 (1984) 408-14.
- 4. Dominguez-Rodriguez, A., Lagerlof, K. K. & Heuer, A., Plastic deformation and solid solution hardening of  $Y_2O_3$ stabilized ZrO<sub>2</sub>. *J. Amer. Ceram. Soc.*, 69 (1986) 281-4.
- Lankford, J., Inverse strain rate effects and microplasticity. *J. Mater. Sci. Lett.*, 8 (1989) 947-9.
- 6. Alexandrov, V. I., Osiko, V. V., Prokhorov, A. M. & Tatarintsev, V. M., Fabrication of high-temperature materials by the direct high-frequency skull-melting technique. *Uspekhi Khimii,* 13 (1978) 386-427.
- 7. Ingel, R. & Lewis, D., Elastic anizotropy in zirconia single crystals. *J. Amer. Ceram. Soe.,* 71 (1988) 265-71.
- 8. Saiki, A., lshisawa, N., Misutani, N. & Kato, M., SEM observation of the stress-induced transformation by Vickers indentation in Y-PSZ crystals. *J. Amer. Ceram. Soe. Jap. Int. Edn,* 97 (1989) 41-6.
- 9. Vircar, A. V. & Matsumoto, R. L. K., Ferroelastic domain switching as a toughening mechanism in tetragonal zirconia. *J. Amer. Ceram. Soe.,* 69 (1986) 224-6.
- 10. Heuer, A., Lanteri, V. & Dominguez-Rodriguez, A., Hightemperature precipitation hardening of  $Y_2O_3$  partially stabilized ZrO<sub>2</sub> (Y-PSZ) single crystals. *Acta Metall.*, 37  $(1989)$  559-67.
- 11. Green, D. J., Hannink, R. H. J. & Swain, M. V., *Transformation Toughening of Ceramics.* CRC Press, Inc., Boca Raton, Florida, 1989.
- 12. Gogotsi, G. A., Drosdov, A. V. & Pejchev, V. G., Mechanical behavior of zirconium dioxide crystals partially stabilized with yttrium oxide. Strength of materials. *Problemy Prochnosti* (1) (1991) 86-91.
- 13. Gogotsi, G. A., Lomonova, E. E. & Osiko, V. V., Studies mechanical characteristics of zirconia single crystals for structural application. *Ogneupory*, (8) (1991) 14–17.
- 14. Gogotsi, G. A., The problem of certification of engineering ceramic by strength characteristics. *Vestnik Mashinostroyenia,* (8) (1989) 27-33.
- 15. Gogotsi, G. A., Deformation behavior of ceramics. *J. Eur. Ceram. Soc.,* 7 (1991) 87-92.
- 16. Gogotsi, G. A., Drosdov, A. V., Zavada, V. P. & Swain, M. V., Comparison of the mechanical behavior of zirconia partially stabilized with yttria and magnesia. *J. Aust. Ceram. Soc.,* 27 (1991) 38-49.
- 17. Quinn, G. D., Flexure testing of advanced ceramics. *Brit. Ceram. Trans. J.,* 88 (1989) 94.
- 18. Strawley, J. E., Wide-range stress intensity factor expression for ASTM E-399 standard fracture toughness specimens. *Int. J. Fracture, 12 (1979) 475-6.*
- 19. Niihara, K., Morena, R. & Hasselman, D. P. H., Evaluation of  $K_{1c}$  of brittle solids by the indentation method with low crack-to-indent ratios. *J. Mater. Sci. Lett.,* 1 (1982) 13-16.
- 20. Adams, J. W., Nacamura, H. H., Ingel, R. & Rice, R. W., Thermal expansion behavior of single crystal zirconia. J. *Amer. Ceram. Soc.,* 68 (1985) 228-31.
- 21. Martinez-Fernandez, J., Jimenez-Melendo, M., Dominguez-Rodriguez, A. & Heuer, A., Elevated temperature studies of microindentation of Y-PSZ structural ceramics. In *Structural Ceramics--Processing Microstructural and Properties,* ed. J. J. Bentzen *et aL* Riso National Laboratory, Roskline, Denmark, 1990, pp.  $413 - 18.$
- 22. Gogotsi, G. A., Deformation and fracture of zirconia ceramics. In *Mechanics and Physics of Fracture of Brittle Materials.* IPM AN Ukr. SSR, Kiev, 1990, pp. 59-66.
- 23. Gogotsi, G. A., Lomonova, E. E. & Ostrovoy, D. Yu., Deformation of ZrO<sub>2</sub> single crystals. *Ogneupory*, (3) (1992) 15-19.
- 24. Lankford, J., Page, R. A. & Rabenberg, L., Deformation mechanism in yttria-stabilized zirconia. *J. Mater. Sci.,* 23 (1988) 4144-56.
- 25. Swain, M. V. & Rose, L. R. F., Strength limitation of transformation-toughened zirconia alloys. *J. Amer. Ceram. Soc.,* 69 (1986) 511-18.
- 26. Gogotsi, G. A., On classification of low-deformable materials by their loading behavior. *Problemy Prochnosti,*  (1) (1977) 77-87.
- 27. Li, Z., Chosh, A., Kobayashi, A. S. & Bradt, R. C., Indentation fracture toughness of sintered silicon carbide in the Palmqvist crack regime. *J. Amer. Ceram. Soc.,* 72 (1989)  $904 - 11$
- 28. Pajares, A., Guiberteau, F., Dominguez-Rodriguez, A. & Heuer, A. H., Microhardness and fracture toughness anisotropy in cubic zirconium oxide single crystals, *J. Amer. Ceram. Soc.,* 71 (1988) 322-33,
- 29. Pajares, A., Guiberteau, F., Dominguez-Rodriguez, A. & Heuer, A. H., Indentation-induced cracks and the toughness anisotropy of 9'4mol%-yttria-stabilized cubic zirconia single crystals. *J. Amer. Ceram. Soc.,* 74 (1991) 859-91.
- 30. Lawn, P., Marshall, D. B., Chautikul, P. & Antstis, G. R., Indentation fracture: Applications in the assessment of strength of ceramics. *J. Aust. Ceram. Soc.,* 16 (1980) 4-9.
- 31. Claussen, N., High-temperature strengthening of zirconiatoughened ceramics. In *Science of hard materials,* ed. E. A. Almond, C. A. Brookes & R. Warren. Adam Holder Ltd, NY, 1989, pp. 377-99.
- 32. Kobayashi, A. S., Matsunuma, K. & Ikawa, H., Evaluation of static and dynamic fracture toughness in ceramics. *Engin. Fract. Mech.,* 31 (1988) 873-85.