JOURNAL OF MATERIALS SCIENCE 28 (1993) 4503–4509

Polycrystalline t′-$ZrO_2(Ln_2O_3)$ formed by displacive transformations

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ZrO_2 (3 mol% Y_2O_3) tetragonal and t′-ceramics (displacively formed ceramics) were compared with ZrO_2 ceramics (3 mol% Ln_2O_3, where Ln = La, Pr, Nd, Sm, Gd, Tb, Dy, Er, or Yb) processed in an identical manner. Sintering at 1500 °C for 2 h produced mainly tetragonal polytypes for the dopants with smaller ionic radii than Dy(i.e., Er, Y and Yb) but when ZrO_2 was reaction sintered with dopants with larger ionic radii excessive monoclinic phase transformation and associated microcracking resulted. High-temperature annealing in the cubic stability regime and rapid cooling through the tetragonal stability regime was used to fabricate t′-composites of ZrO_2 doped with Y, Yb, Er or Dy. Room-temperature fracture toughness and strength values are explained on the basis of a ferroelastic-cubic-to-tetragonal transformation. The domain structure was viewed by transmission optical microscopy (TOM) or transmission electron microscopy (TEM).

1. Introduction

Wadhawan [1] in a review article on ferroelasticity suggested that ferroelastic switching during the monoclinic-to-tetragonal transformation in zirconia ceramics may contribute to their toughness in addition to the well-documented transformation toughening [2] in these materials. Michel *et al.* [3] studied skull-melted polydomain ZrO_2 single crystals doped with Y, Gd or Yb and found that these t′ (displacively formed) crystals had higher toughnesses than cubic ZrO_2 (9 mol% Y_2O_3) crystals. They attributed the higher toughnesses to ferroelastic domains giving rise to textures due to crack deflection. Virkar and Matsumoto [4, 5] suggested that toughening in fine-grained, tetragonal-zirconia-polycrystalline (TZP) ceramics was due in part to ferroelastic domain switching, based on textures observed by X-ray diffraction (XRD). They suggested that this energy-absorbing mechanism was not limited to TZP materials but was a feature of a wide variety of ferroelastics. Subsequent studies [6–13] have verified that ferroelastic toughening is a viable toughening mechanism in a variety of materials.

One of the most interesting results of this recent research is the study of displacively formed t′-zirconia materials. Large-grained (50–150 μm) polycrystalline t′-ZrO_2 can be formed by annealing polycrystalline zirconia in the cubic stability regime ($\geqslant$2050 °C for ZrO_2 (3 mol% Y_2O_3)) and rapidly cooling through the cubic-to-tetragonal-transition temperature. Jue and Virkar [8] showed that these large-grained materials have toughnesses similar to fine-grained-transformation-toughened Y-TZP materials, despite the fact that the t′-high-temperature-processed materials did not transform to monoclinic ZrO_2. Both the tetragonal materials (t-materials) and t′-materials had toughness two to three times greater than cubic zirconia (c-zirconia), which is neither transformation nor ferroelastic toughened. Switching of submicrometre domains was identified as the reason for toughening in the polycrystalline t′-materials; and domain size, not grain size, controls whether the ZrO_2 remains tetragonal upon cooling into the monoclinic stability regime. A subsequent study by Jue *et al.* [11] showed that domain growth can occur upon switching and that a critical domain size can be achieved so that switching triggers transformation.

While the polycrystalline t′-materials display high toughness and good resistance to low-temperature ageing (i.e., transformation), their large grain size limits their strength, as expected. Sintering at temperatures above 2100 °C in an oxidizing environment is not practical for many applications. The purpose of this paper is to report on an effort which explored the feasibility of lowering the annealing temperature for t′-zirconia polycrystalline ceramics by substituting

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lanthanide oxides for Y_2O_3, as well as investigating the feasibility of annealing these materials for short times in a graphite furnace.

2. Experimental procedure

Compositions were prepared by the vibratory milling of ZrO_2 (Daiichi DK-1) in methanol (using $ZrO_2(MgO)$ media) with either 3 mol % Y_2O_3 (Molycorp 5600) or 3 mol % Ln_2O_3, where Ln = La, Pr, Nd, Sm, Gd, Dy, Er, or Yb. The lanthanide oxides (Molycorp) were generally purer than 99.9%. The powders were vibratory milled for 16 h, followed by wet screening through a 45 μm screen and dry screening through a 80 μm screen. The powders were uniaxially dry pressed at 35 MPa into bar-shaped and rod-shaped samples and then isostatically pressed at 200 MPa.

The pressed bars were sintered at 1500 °C for 2 h in air. Compositions were subsequently cladless hot isostatically pressed (cladless HIPed) at 1550 °C for 30 min in 200 MPa Ar. High-temperature annealings were performed in a ZrO_2 (3 mol % Y_2O_3) crucible inside a graphite-resistance-heated furnace, by rapidly heating ($\sim$75–100 °C min^{-1}) above 1000 °C to the desired annealing temperature in Ar. The hold time at temperature was 5 min or less. The cooling rate was $\sim$100 °C min^{-1} to 1500 °C. Samples were reoxidized by heating to 1000 °C in air at a rate of 80 °C h^{-1} and held at temperature for 2 h before examination using transmission optical microscopy (TOM) and transmission electron microscopy (TEM). TOM specimens were viewed under cross-polarized light after dimpling and polishing to a thickness of 10–15 μm. TOM samples were subsequently ion-beam milled for TEM analysis.

The density was measured by water displacement. Sintered bars were X-rayed and subsequently ground using a 220 grit diamond wheel. Four-point bend strength was measured using a universal testing machine with a cross-head speed of 0.05 mm min^{-1}, a support span of 40 mm and a loading span of 20 mm. The fracture toughness was measured using the short-rod technique [14] on 12.5 mm diameter samples. Ground, polished and fractured samples were X-rayed to determine the ZrO_2 polytypes present [15] and to examine switching. The hardness was determined using a 75 N indent made with a Vickers 136° diamond indenter on polished surfaces.

3. Results and discussion

3.1. Sintering and hot isostatic pressing

The green densities of the pressed samples were only 46–48% of the theoretical values. These low values were the result of the high surface area and poor packing of the powder. Sintered densities ranged between 90% of theoretical ($ZrO_2(La_2O_3)$) to 99% of theoretical ($ZrO_2(Dy_2O_3)$) as shown in Table I. ZrO_2 sintered with Y_2O_3, Dy_2O_3, Er_2O_3 or Yb_2O_3 had closed porosity after sintering. Open porosity, mainly due to microcracking, resulted in a decrease, rather than an increase in density after hot isostatic pressing (HIPing) for ZrO_2 sintered with La, Pr, Nd and Sm. ZrO_2 (3 mol % Gd_2O_3) had mainly closed porosity after sintering, as evidenced by the increase in density upon HIPing, but visual cracks were observed after sintering due to the large amount of monoclinic zirconia (m-zirconia) (see Table I). Dy, Y, Er, and Yb-TZP samples had densities greater than 99% of the theoretical value after HIPing. These samples had no visual cracks despite relatively high amounts of m-ZrO_2 (7–13%) and were therefore used for the high-temperature heat treatments.

TABLE I Sintering behaviour of ZrO_2 (3 mol % Ln_2O_3) in air at 1500 °C

Dopant	Density sintered	(% TD[a]) HIPed	t (%)	Comments
La_2O_3	90.0	86.5	0.0	Severely cracked
Pr_2O_3	92.2	90.0	0.0	Several cracks
Nd_2O_3	92.1	89.7	24.9	Some cracks
Sm_2O_3	92.3	92.3	21.3	Several cracks
Gd_2O_3	93.8	98.2	70.6	Cracks
Dy_2O_3	98.7	100.0	88.1	No cracks
Y_2O_3	97.1	99.2	93.3	No cracks
Er_2O_3	98.2	100.0	92.5	No cracks
Yb_2O_3	95.4	100.0	86.9	No cracks

[a] Percentage of the theoretical density.

It is widely recognized that the ionic size of the dopant affects the stabilization of ZrO_2 [16, 17]. The closer the ionic size is to Zr^{+4}, the easier the stabilization. In the case of lanthanide-series dopants, the lower the ionic size, the closer the mismatch in size between Zr and Ln. The fact that large ions can go into solution with Zr is evidenced by effective stabilization of zirconia with Ca or La [2]. The present results, however, show the difficulty of stabilizing t-ZrO_2 by doping with large ions using reaction sintering.

A problem with reaction sintering (as opposed to calcining, milling, and sintering the tetragonally stabilized powder) is the volume change associated with transformation of the c-lanthanides to either m-polymorphs or hexagonal polymorphs (h-polymorphs) [18] prior to reaching temperatures where solid-state diffusion can occur. Reaction sintering was effective for dopants with c-structures stable up to the sintering temperature (i.e., Y, Yb, Er or Dy), whereas dopants which transformed from cubic to monoclinic (i.e., Sm or Gd) or from cubic to hexagonal (i.e., La, Pr or Nd) showed visual cracks after sintering. It is possible that some of these cracks occurred during heating due to phase transformation of the dopants.

The use of coprecipitated powders, improved dispersion of the dopant, a more reactive ZrO_2, or the addition of a calcination step would probably overcome the sintering problems observed in the present study. However, the ZrO_2 compositions which sintered well were those with the lowest Curie temperatures (see Table II) and those which were most desired. Rouanet [19] showed that the cubic-to-tetragonal transformation temperature was lowered with decreasing ionic radius of the lanthanide-oxide

TABLE II Tetragonal-to-cubic transformation temperature for ZrO_2 (3 mol % Ln_2O_3) [19, 20]

Dopant	Approximate Curie temperature (°C)
La_2O_3	2140
Pr_2O_3	2095
Nd_2O_3	2095
Sm_2O_3	2070
Gd_2O_3	2045
Tb_2O_3	2030
Dy_2O_3	2030
Y_2O_3	2000
Er_2O_3	2000
Yb_2O_3	1950

TABLE III Comparison of HIPed (t + m) and annealed (t') ZrO_2 (3 mol % Ln_2O_3) compositions

Dopant	Density (% TD[a])		t or t' (%)		Grain size (μm)	
	1500 °C	2200 °C	1500 °C	2200 °C	1500 °C	2200 °C
Dy_2O_3	100	99.7	88.1	100	0.7	50
Y_2O_3	99.2	99.0	93.3	100	0.7	50
Er_2O_3	100	99.7	92.5	100	0.7	45
Yb_2O_3	100	99.7	86.9	100	0.7	60

[a] Percentage of the theoretical density.

TABLE IV Comparison of hardness and switching in HIPed (t + m) and annealed (t') ZrO_2 (3 mol % Ln_2O_3)

Dopant	T_c (°C)	Hardness (GPa)		XRD [(0 0 2)/(2 0 0)][a]	
		1500 °C	2200 °C	Hand[b]	Machine[c]
Dy_2O_3	~ 2030	9.0	11.1	1.4	4.4
Y_2O_3	~ 2000	11.5	11.3	1.4	2.6
Er_2O_3	~ 2000	11.6	11.7	1.5	4.9
Yb_2O_3	~ 1950	11.1	11.3	2.1	3.8

[a] XRD of samples annealed at 2200 °C. The values represent the ratio of (0 0 2)/(2 0 0) peak integrated intensities on ground/polished surfaces (the higher the values, the more switching has occurred).
[b] Moderate pressure via hand grinding.
[c] Surface grinding under typical finish-grinding conditions.

additive in solution with ZrO_2. The equilibrium temperature between the c-polymorphs and t-polymorphs of 3 mol % ZrO_2 compositions [19, 20] is given in Table II. In order to form t'-materials, it is necessary to heat above this temperature and then rapidly cool to retain the displacively formed t'-domain structure.

3.2. High-temperature heat treatments

Upon annealing ZrO_2 (3 mol % Dy_2O_3, Y_2O_3, Er_2O_3, or Yb_2O_3) at 2000 °C for 5 min, only the ZrO_2-(Yb_2O_3) composition avoided microcracking. This is consistent with the lower tetragonal-to-cubic transformation temperature for this composition, as compared to the compositions partially stabilized with Dy_2O_3, Y_2O_3 or Er_2O_3. If the sample does not reach the cubic stability range, the rapid grain growth which occurs upon heating results in transformation from tetragonal to monoclinic (and associated microcracking) upon cooling. As expected, by heating to 2200 °C it was possible to obtain crack-free Dy_2O_3, Y_2O_3 or Er_2O_3 partially stabilized ZrO_2 short-rod samples.

A comparison between the sintered compositions and the samples 2200 °C annealed in Ar and then reoxidized is given in Table III. The density was essentially unaffected by the high-temperature annealing but the grain size increased dramatically and the samples were t' rather than t + m (see Tables III and IV). The formation of t'-grains, despite the large grain size, is in accord with the work of Jue and co-workers [8, 11] for $ZrO_2(Y_2O_3)$ annealed for much longer times in air at 2100 °C. The hardness of the t'-materials was similar to that of t-ZrO_2, despite the increase in grain size of approximately two orders of magnitude (see Table IV). Grinding caused switching in all four t'-materials with no substantial differences between the four materials after surface grinding with a downfeed of 5 μm pass^{-1}. The ZrO_2 (3 mol % Yb_2O_3) showed a greater tendency to switch than the other materials when only hand pressure was applied (see Table IV), but quantitative experiments are required to see if the onset of switching occurs more readily with this material.

TOM showed domain structure in all four materials, as expected. The resolution using TOM, as shown in Fig. 1, is not adequate to distinguish differences in domain size between the four materials. A cursory attempt to do so was made using TEM. Bright-field TEM micrographs delineating twins in grains oriented along the [1 1 0] zone axis are shown in Fig. 2. Selected-area diffraction showed no monoclinic ZrO_2, as expected on the basis of the XRD data. The domain size (twin spacing) was ~ 0.1 μm for the ZrO_2 containing Dy_2O_3, Y_2O_3, or Er_2O_3, but appeared less (~0.06 μm) for the ZrO_2 (3 mol % Yb_2O_3) samples. Further TEM work is required to verify the differences, if any, in domain size.

The microstructural differences between the four materials were minimal. Yoshimura [21] has shown that partially stabilized ZrO_2 (Ln_2O_3) materials have similar tetragonality at a given concentration of Ln_2O_3. It is, therefore, not surprising that all four t'-ZrO_2 compositions result in similar microstructures.

3.3. Strength and fracture toughness

The strength of t'-composites was significantly decreased in relation to the as-HIPed strengths, as shown in Fig. 3, due to the larger grains acting as stress concentrators. The strength of the HIPed ZrO_2 (3 mol % Y_2O_3), however, was low in comparison to commercially available ZrO_2 (3 mol % Y_2O_3) (TOSOH TZ-3Y), which when sintered, HIPed and tested in a similar manner, resulted in a strength of 1457 ± 134 MPa [13]. It is well recognized that the processing of ceramics plays a key role in determining their strength and that typical defects (agglomerates, pores, surface cracks, inclusions, etc.) limit the strength

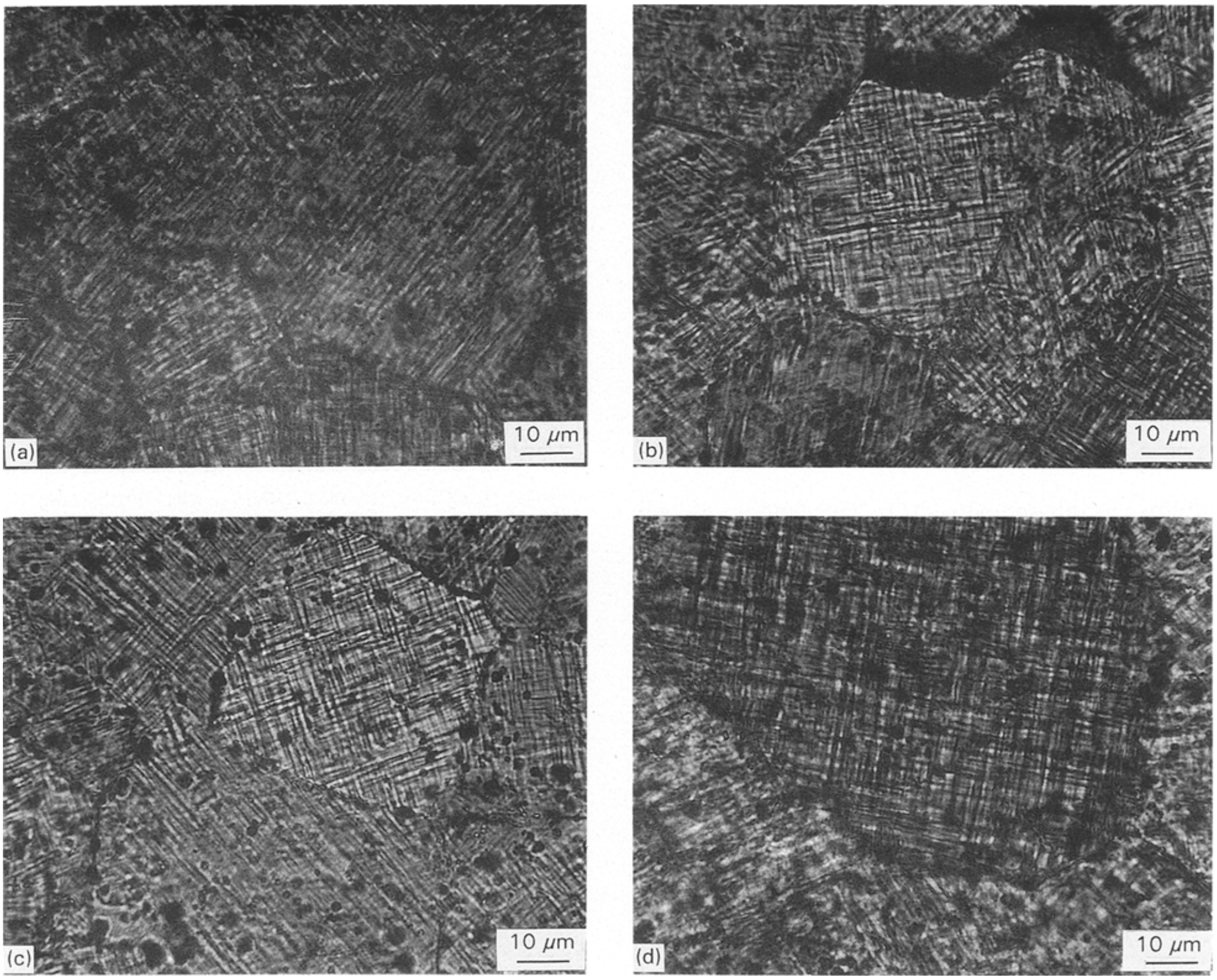

Figure 1 TOM micrographs of t'-ZrO_2 (3 mol % Ln_2O_3) annealed at 2200 °C in Ar and reoxidized at 1000 °C. Note the domain structure visible in cross-polarized light. (a) Ln = Dy, (b) Ln = Y, (c) Ln = Er, and (d) Ln = Yb.

in fine-grained ceramics [22, 23]. The reason for the lower strength of HIPed ZrO_2 (3 mol % Yb_2O_3) was not obvious by fractography but it is probably related to agglomerate size and shape, and their packing during pressing.

Despite the lower strength of the t'-materials relative to the HIPed compositions, it is interesting to observe that the strength values are still considerably higher than for c-ZrO_2. A commercially available ZrO_2 (8 mol % Y_2O_3) (TOSOH TZ-8Y) sintered, HIPed and tested in a similar manner to the above bars resulted in a strength of 211 ± 21 MPa [13] despite a grain size five times smaller than the t'-materials. X-ray analysis of fractured t'-ZrO_2 bars showed no monoclinic formation and therefore transformation toughening could only have been operative if reverse transformation occurred. The higher strength of t'-bars in comparison to c-ZrO_2 is believed to be related to the higher toughness of t'-ZrO_2 relative to c-ZrO_2.

The toughness of sintered (1500 °C) or HIPed (1550 °C) transformation-toughened materials was compared with nontransformation-toughened t'-materials annealed either at 2000 °C (Yb doped in Fig. 4a) or 2200 °C (Dy, Y, or Er doped in Fig. 4b). As mentioned above, the cracking associated with the 2000 °C annealing of Dy-, Y-, or Er-doped zirconias was related to grain growth causing the tetragonal-to-monoclinic transformation and associated microcracking, whereas the Yb-doped at 2000 °C and all of the 2200 °C materials consisted entirely of t'-ZrO_2 since they had been heated into the cubic stability regime. Dy-doped ZrO_2 had the highest toughness, and Yb-doped ZrO_2 the lowest toughness, although the differences were not substantial.

The short-rod bulk toughness of the t'-materials is very similar to the transformation-toughened materials. However, c-ZrO_2 (8 mol % Y_2O_3) had a toughness of 1.5–1.8 MPa $m^{\frac{1}{2}}$ when compared by the same technique [13]. No m-ZrO_2 was detected by XRD in the t'-ZrO_2(Ln_2O_3) ceramics, consistent with the earlier work of Jue and Virkar which showed that ZrO_2 (3 mol % Y_2O_3) annealed in air at >2100 °C showed no signs of a reversible transformation [8]. Jue and Virkar found that the toughnesses of t'-ZrO_2 (3 mol % Y_2O_3) samples were about three times greater than c-ZrO_2 (8 mol % Y_2O_3) using the single-edge-notch-bend (SENB) technique for fracture toughness. The short-rod measurements resulted in values for the t'-materials which were two to three times higher than

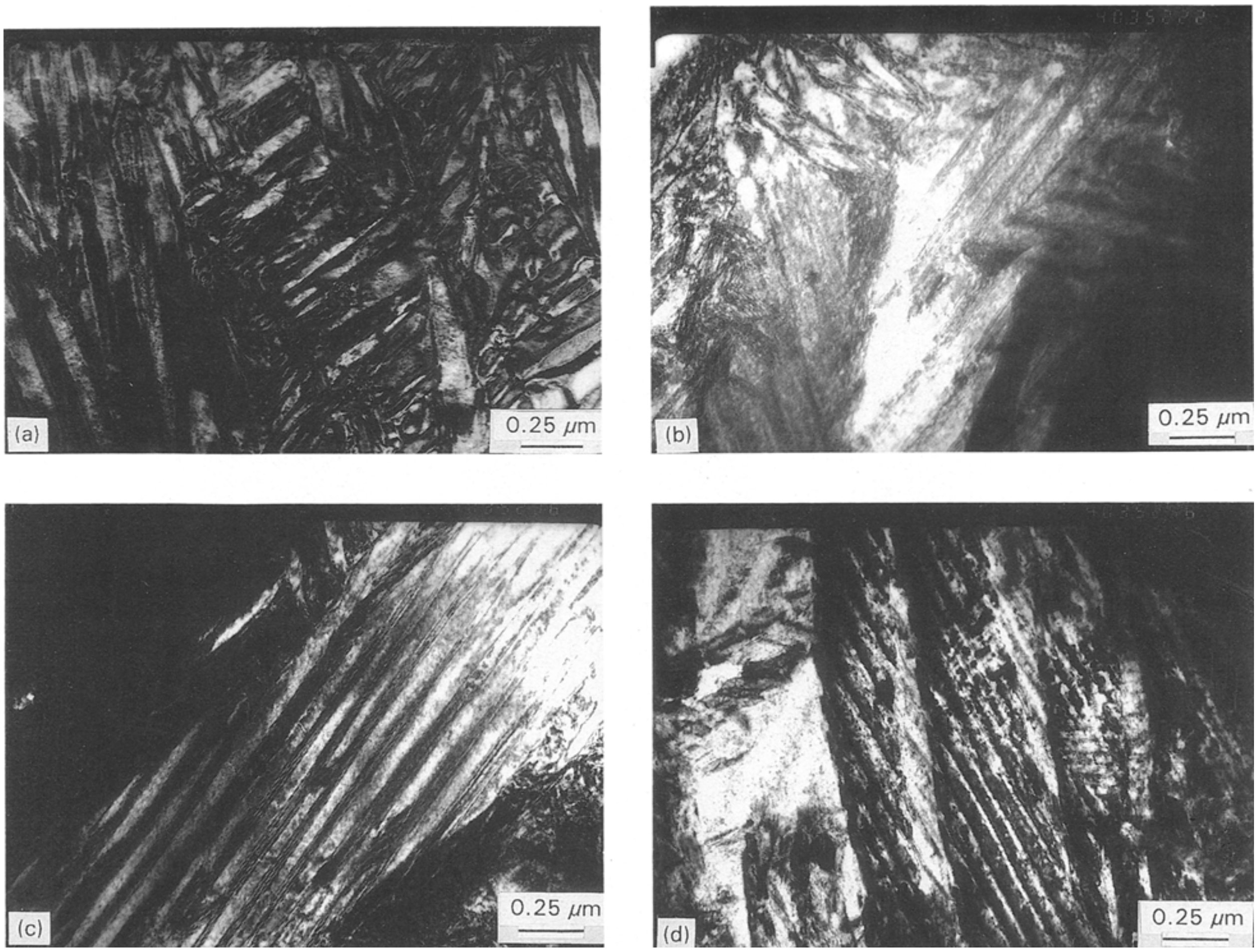

Figure 2 TEM micrographs of t'-ZrO_2 (3 mol % Ln_2O_3) annealed at 2200 °C in Ar and reoxidized at 1000 °C. Note the domains in grains oriented along the [1 1 0] zone axis. (a) Ln = Dy, (b) Ln = Y, (c) Ln = Er, and (d) Ln = Yb.

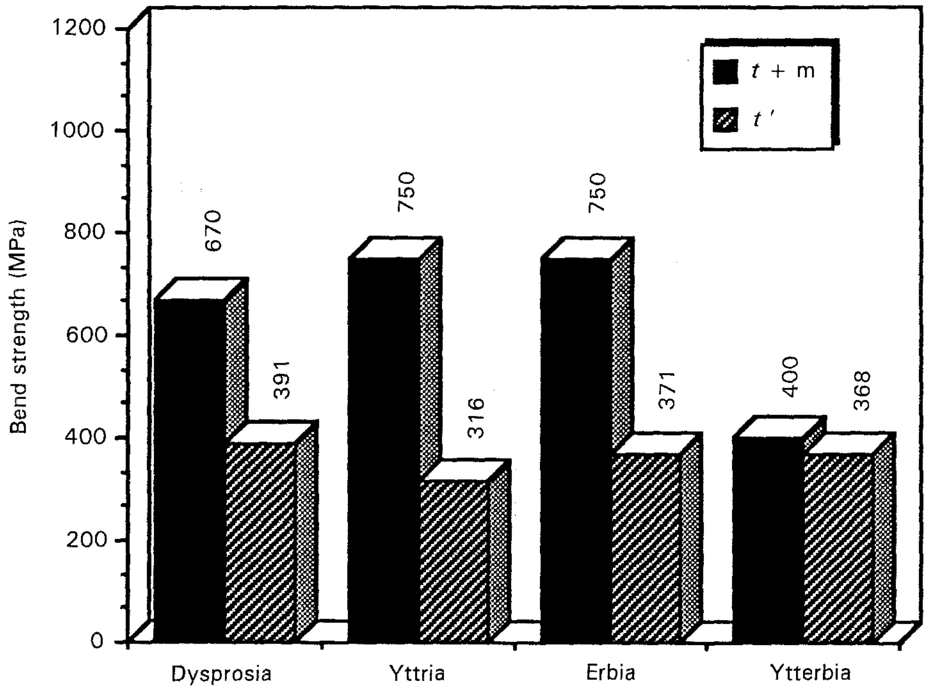

Figure 3 Strength comparison of sintered (t + m, HIPed at 1550 °C) and annealed (t', heat treated at 2200 °C) ZrO_2 (3 mol % Ln_2O_3).

for c-ZrO_2 [13] and only slightly lower in toughness than transformation-toughened ZrO_2. This is consistent with the conclusions of Virkar *et al.* [12] that ferroelastic switching can play a significant role in toughening ceramics.

4. Conclusion

Polycrystalline t'-ZrO_2 (3 mol % Dy_2O_3), ZrO_2 (3 mol % Er_2O_3), and ZrO_2 (3 mol % Yb_2O_3) were all successfully fabricated by heating them into the cubic stability range (> 2000 °C) and cooling at rates of

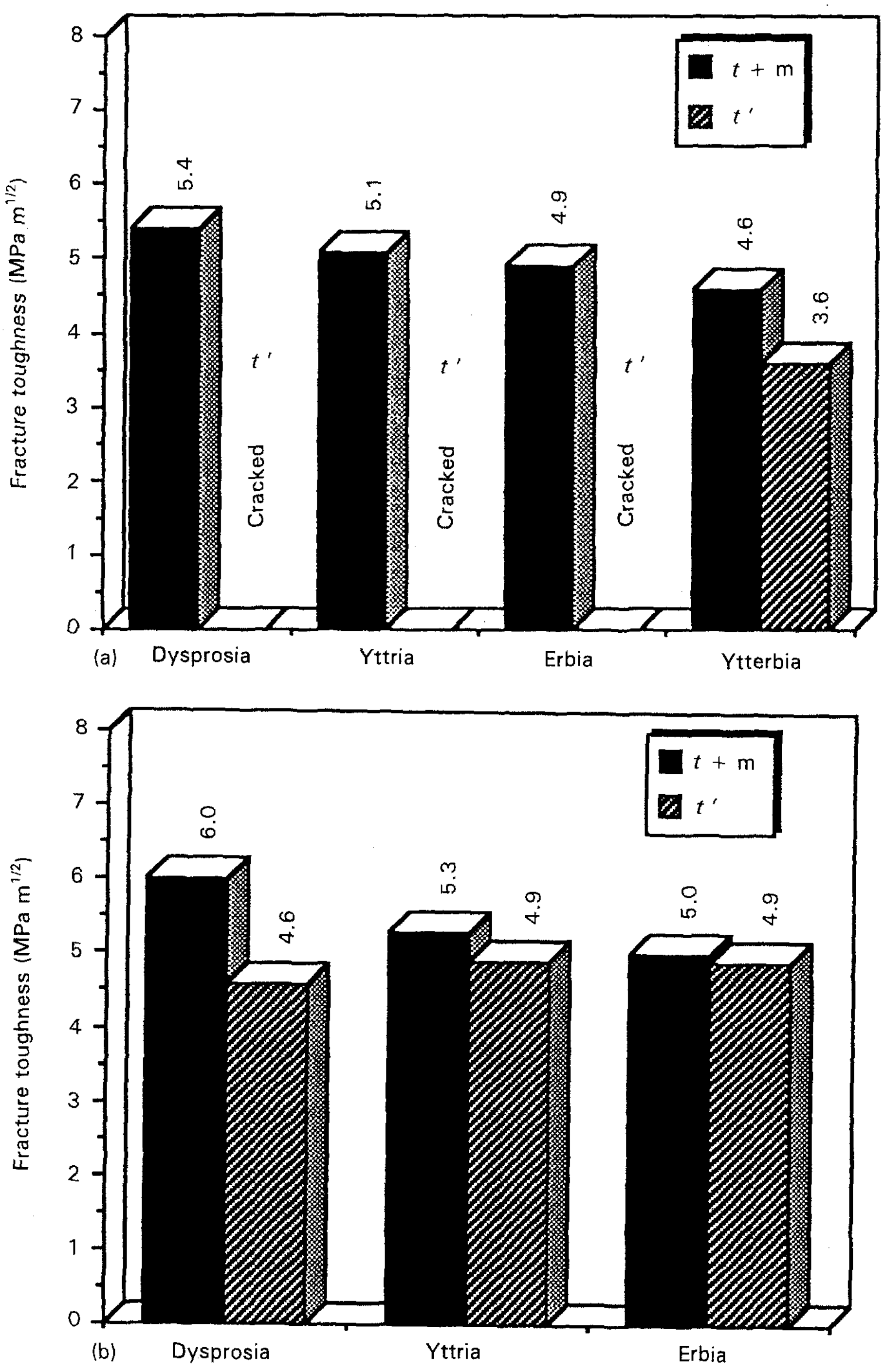

Figure 4 Short-rod-fracture-toughness comparison of sintered (t + m) and annealed (t′) ZrO_2. (a) Sintered in air at 1500 °C (t + m) and sintered samples annealed at 2000 °C for 5 minutes (t′), (b) samples HIPed at 1550 °C (t + m) and HIPed samples annealed at 2200 °C for 5 min (t′).

~ 100 °C min^{-1}. These materials have domain structures similar to t′-ZrO_2 (3 mol % Y_2O_3) based on TOM and TEM. Domain switching after surface grinding was also similar for all four materials.

High-temperature-annealed t′-zirconias have similar toughnesses to their transformation-toughened counterparts and are two to three times tougher than c-ZrO_2. The high toughness in t′-materials, relative to c-ZrO_2, was attributed to ferroelastic switching since transformation toughening is not operative in these materials.

The hardness of the 45–60 μm grain size t′-zirconias was similar to that of the 0.7 μm grain size HIPed materials. The strength of t′-materials decreased dramatically in comparison to the sintered and HIPed materials due to the increase in grain size. However, strengths on the order of 300–400 MPa are still significantly higher than those measured for c-zirconia with a finer grain size. The higher strength is believed to be due to the increased toughness of these materials.

No significant advantage was observed when substituting lanthanide oxides for Y_2O_3 in t′-zirconias. The lower tetragonal-to-cubic transition temperature did not result in a dramatically improved strength since rapid grain growth occurs at temperatures of 2000 °C. Short-term exposures to the reducing environment of graphite furnaces did nothing more than change the colour of the ceramic from white to black and can be used to form t′-ceramics. Rapid sintering (e.g. by microwave) in air, however, should be investigated as an alternative route for synthesizing finer-grained t'-Y-ZrO_2 in an effort to achieve better strengths.

Acknowledgement

This work was supported by the Defense Advanced Research Projects Agency (DARPA) through AFOSR under Contract No. F49620-89-C-0054.

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Received 2 June 1992
and accepted 11 January 1993