Available online at www.sciencedirect.com

ScienceDirect

Journal of the European Ceramic Society 31 (2011) 1009–1014

www.elsevier.com/locate/jeurceramsoc

Original Article

Zirconia–multiwall carbon nanotubes dense nano-composites with an unusual balance between crack and ageing resistance

N. Garmendia[a,b,*], S. Grandjean[c], J. Chevalier[c], L.A. Diaz[d], R. Torrecillas[d], I. Obieta[a,b]

[a] *TECNALIA, San Sebastian E20009, Spain*
[b] *CIBER-BBN, San Sebastian E20009, Spain*
[c] *MATEIS UMR CNRS 5510, INSA-Lyon, Université de Lyon, Villeurbanne Cedex 69621, France*
[d] *Nanomaterials and Nanotechnology Research Center (CINN), Principado de Asturias – Consejo Superior de Investigaciones Científicas (CSIC) – Universidad de Oviedo (UO), Parque Tecnológico de Asturias, Llanera E33428, Spain*

Received 3 September 2010; received in revised form 13 December 2010; accepted 21 December 2010
Available online 21 January 2011

Abstract

Yttria stabilized zirconia (Y-TZP) ceramics are used in a wide variety of applications, such as orthopaedic and dental implants. Y-TZP offers indeed a unique combination of biocompatibility and mechanical properties (high crack resistance for a ceramic). However, the major drawback of Y-TZP is their lack of stability: zirconia is prone to ageing, especially under humid atmosphere. Increasing the ageing resistance of Y-TZP led so far to a decrease of toughness and crack resistance. Here we show that the addition of a small volume fraction of multiwall carbon nanotubes (MWCNT) in a polycrystalline nano-structured Y-TZP sintered under specific conditions (Spark Plasma Sintering) leads to a material exhibiting a balance between ageing and crack resistance never reached before.

Keyword: Nanotube; ZrO_2; Nanocomposites; Biomedical applications; Ageing

1. Introduction

Yttria stabilized zirconia (often referred as ‘Y-TZP’) ceramics are widely used for medical devices such as orthopaedic and dental implants. Y-TZP offers a unique combination of biocompatibility and mechanical properties (high crack resistance for a ceramic). Zirconia presents a reinforcement mechanism by phase transformation that gives excellent mechanical properties to the ceramic material.[1,2] However, the major drawback of Y-TZP is its lack of stability: zirconia is indeed prone to ageing especially (but not only) under humid atmosphere. Ageing is referred to a slow surface transformation of the zirconia from its high temperature structure (tetragonal structure), obtained by the stabilization of the ceramic with yttria, into the stable monoclinic phase in the presence of water or water vapor. This transformation induces surface roughening, microcracking and for the most severe cases failure and loss of functionality.[3] The most dramatic case of ageing was reported at the beginning of 2002 for zirconia hip joint heads, when several hundreds of implants failed within a short period. There have been several attempts in the recent literature to increase the ageing resistance of Y-TZP. However, increasing the ageing resistance of Y-TZP led so far to a decrease of toughness and crack resistance. To avoid the ageing it is necessary to reduce the transformability of the zirconia, reaching a more stable tetragonal phase. This will also imply less transformability under stress, which results in lower mechanical strength. The reduction of the zirconia grain size to a submicrometric or nanometric level, limits the phase transformation and, therefore, ageing is delayed.[4,5] Anyhow, the fracture toughness is reduced, because the transformation toughening mechanism is lost.

Since carbon nanotubes (CNT) were first described by Iijima in 1991,[6] there has been a growing interest on the use of the exceptionally stiff and strong CNT as reinforcements in ceramic matrix materials.[7–11] However, as pointed out by Padture in a recent short survey, the clear demonstration of the toughening effect of the carbon nanotube in ceramic matrix composites remains elusive.[12] Some authors who have worked with MWCNT do not demonstrate a real improvement on the

---

* Corresponding author at: TECNALIA, San Sebastian E20009, Spain.
Tel.: +34 943003700; fax: +34 943003800.
E-mail address: nere.garmendia@tecnalia.com (N. Garmendia).

0955-2219/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2010.12.029

mechanical properties of the nanocomposites. Sun et al.[13] concluded that the addition of CNT does not result in enhanced hardness and fracture toughness of their composites, although the addition of MWCNT showed better performance than the addition of SWCNT. Duszová et al.[14] found that their nanocomposites exhibited an enhanced hardness and toughness compared to monolithic materials, but they did not obtain a good density of the ZrO_2–CNT composites (due to the clusters of carbon nanotubes). Ukai et al.[15] also found little improvement with the addition of MWCNT to the ZrO_2 matrix. All these authors confirm that to enhance the mechanical properties of the CNT/nanozirconia composite it is critical to have a chemical bonding between the nanotube and the zirconia matrix and to ensure a good dispersion of the CNT. Padture[12] focuses his work in the toughening mechanisms of nanocomposites of ceramics with singlewall carbon nanotubes (SWCNT). He claims that these nanocomposites present unique grain boundaries, containing 1-D tortuous SWCNT bundles that form 2-D tangled embedded nets. What appears to be occurring with the nanoscale, flexible SWCNT is the uncoiling of the grain-boundary CNT bundles in the crack wake, as the crack advances intergranularly. With further propagation of the crack, the uncoiled SWCNT would stretch, as long as both ends are anchored or embedded in the grain boundary, so the crack propagation is impeded. Eventually, the CNT bridges will pullout or detach. The stretched SWCNT bridges will be really effective if they became tight immediately after the crack tip. But if the stretched-SWCNT bridging is aimed to be the dominant toughening mechanism, it is imperative that the SWCNT net is anchored to the grains by a strong interface and provides weakness within the net, allowing intergranular crack propagation. Although the cited article is limited to ceramic/SWCNT composites, the described mechanisms might be applied to composites containing MWCNT which present the same type of grain-boundary structures. Therefore, Padture agrees with the above-mentioned authors that to really reach an enhancement in toughness it is essential to have a bonding with the zirconia and the nanotubes and a good dispersion. Padture's observations of bridging by CNT are now a clear demonstration of the capacity of CNT to reinforce ceramics. However, a quantification of this effect is still lacking.

In this work, we show that the addition of a small volume fraction of multiwall carbon nanotubes (MWCNT) in a polycrystalline, nano-structured Y-TZP, sintered under specific conditions (Spark Plasma Sintering) leads to a material exhibiting a balance between ageing and crack resistance never reached before.

2. Materials and methods

The starting materials were zirconia partially coated MWCNT and commercial yttria stabilized nanozirconia (Inframat Advanced Materials, USA) with a primary particle size of 30–60 nm and a specific surface area 41.7 $m^2\,g^{-1}$. The nanozirconia partially coated MWCNT were obtained by hydrothermal synthesis and the existence of a bonding between the MWCNT and the nanozirconia has been proved elsewhere.[16–18] To ensure a good dispersion of the carbon nanotubes in the zirconia matrix the powders were mixed using a heterocoagulation process together with a colloidal processing route and afterwards carefully dried.[19] The percentage of MWCNT ranged from 0 to 5.6 vol.% (0–1.8 wt%).

To limit the degradation of the carbon nanotubes during the sintering process and avoid the grain growth, Spark Plasma Sintering (SPS) was used.[25] The studied samples contained different amounts of MWCNT (0 vol.%, 3 vol.%. and 6 vol.%, with regard to the zirconia volume). The equipment used was a FCT Systeme GmbH (Germany) model HPD-25. The heating ramp was 95 °C min^{-1} up to 600 °C and, then, 85 °C min^{-1} up to the final temperature of 1200 °C. The working atmosphere was low vacuum (10^{-1} mbar) and the cycle lasted 3 min, with a 100 MPa uniaxial pressure applied over the cylindrical graphite dies of 20 mm diameter. Samples were polished with diamond paste.

High Resolution Scanning Electron Microscopy (HRSEM) experiments were carried out in a JEOL JSM-7600F. Atomic Force Microscopy (AFM) experiments were performed in a Digital Instruments Multimode AFM, with a Nanoscope III controller, in tapping mode. The TEM images were obtained with a field emission gun microscope, JEOL 2010F, which works at 200 kV and has a point-to-point resolution of 0.19 nm.

The hardness and the fracture toughness of the samples were measured using the Vickers indentation tests. In this work, the direct measurement of Vickers-produced radial cracks as a function of time was carried out, in order to obtain the evolution of the stress intensity factor and K_{I0}, that will be the K_I value of equilibrium. The cracks were measured immediately after indentation and after 5, 10, 15, and 30 min, 1, 2 and 24 h.

For determining the stress intensity factor (K_I) the following expression by Lawn was used[20]:

$$K_I = \chi \cdot P \cdot c^{-3/2} \tag{1}$$

$$\chi = C \cdot \left(\frac{E}{H}\right)^{1/2} \tag{2}$$

where P is the applied force in Newtons and c is the crack length. χ is a constraint factor defined by Anstis et al.[21] where C is a geometric constant that values 0.016, H is the Vickers hardness in GPa and E is the Young's modulus in GPa. For all the studied samples E was considered to be $E = 210$ GPa, the standard Young's modulus value of the zirconia.[1]

The initial monoclinic content of the samples was close to zero in all cases. Ageing experiments were carried out by keeping samples in a steam autoclave at a temperature of 134 °C for different times. The diamond polished side of each specimen was examined by X-ray diffraction (XRD) before and after ageing. XRD were obtained with a diffractometer using Ni-filtered Cu Kα radiation. The tetragonal/monoclinic zirconia ratio was determined using the integrated intensity (measuring the area under the diffractometer peaks) of the tetragonal (1 0 1) and two monoclinic (1 1 1) and ($\bar{1}$ 1 1) peaks as described by Garvie and Nicholson and then revised by Toraya et al.[22,23] Diffractometer scans were obtained from $2\theta = 27$–$33°$, at a scan speed of 0.2° min^{-1} and a step size of 0.02°.

Table 1
Density, hardness and threshold stress intensity factor of the samples.

Sample	Density (g/cc)	Density (% TD)	Average grain size (nm)	Hardness (GPa)	K_{I0} (MPa × $m^{1/2}$)
TZ-3Y	6.0	98.8	459 ± 62	12.68 ± 0.05	3.81 ± 0.17
SPS-0	6.0	98.7	199 ± 34	13.32 ± 0.19	2.36 ± 0.08
SPS-3	6.0	99.5	218 ± 64	11.52 ± 0.12	4.06 ± 0.17
SPS-6	5.8	99.1	146 ± 26	10.61 ± 0.35	2.07 ± 0.29

3. Results and discussion

In Table 1 the densities of the samples and grain sizes are presented. High density nanocomposite samples were obtained, with densities beyond 99% of the theoretical. The grain sizes range between 100 and 300 nm. For comparison purposes, a pressureless sintered yttria-stabilized zirconia body was studied, with a grain size in the range of 450 nm.

The SPS sintered samples without nanotubes (SPS-0) showed the highest hardness values (HV = 13.32 GPa), with an increase of a 5% when compared to the conventional yttria-stabilized zirconia samples (TZ-3Y). This increase in hardness is explained by the decrease in the grain size. On the other hand, the samples which contained 3 vol.% and 6 vol.% of CNT (SPS-3 and SPS-6, respectively) showed a decrease in hardness. This decrease is more important for the samples with the higher amount of CNT, with a decrease over 16% when compared to the conventional yttria-stabilized zirconia, and more than 20% regarding to the SPS sintered samples without CNT. The same tendency has been shown in previous works, without explanation.[9,14,15] This effect will be the subject of further studies.

The stress intensity factor has been obtained by indentation toughness method. Lately, this method has become very controversial, especially in CNT-ceramic composites.[13,24–28] The work of Mukherjee et al. shows that under some circumstances, cracks are hardly produced at all, giving ridiculously high toughness values when dragged through the equation given. If this is the case, then it could appear that sometimes an overoptimistic value could result even with slow crack growth. Jiang and Mukherjee also support the idea that the indentation test is useful for assessing relative toughness values, if sufficiently developed cracks are produced. In this paper a possible validation of the technique is presented. As it can be seen in the micrographs of Fig. 1, taken 24 h after indentation, the cracks have fully developed. Moreover, we believe that the method is more effective in obtaining the threshold below which no crack propagation occurs, K_{I0}.[29] The K_{I0} value will give the safety range of use of the material in many applications, such as joint prostheses. In Fig. 2 the comparison of the stress intensity factor as a function of the time is presented for the different ceramics. The stress intensity factor first decreases with time. This is related to slow crack growth (SCG). Zirconia, as all oxide ceramics, is indeed prone to SCG, due to stress assisted corrosion by water molecules.[30–32] After a given period crack extension stops (K_I remains constant), which means that K_I has reached the threshold K_{I0} for SGC. The K_{I0} values are reported in Table 1. SPS-0 samples show a low value of K_{I0} compared to TZ-3Y samples. These values are in good agreement with the fact that, in general, fracture resistance is observed to increase with grain size. Indeed, the tetragonal zirconia grain size controls the transformation toughness mechanism and the larger the grain size, the easier the transformation.[33] The samples with the

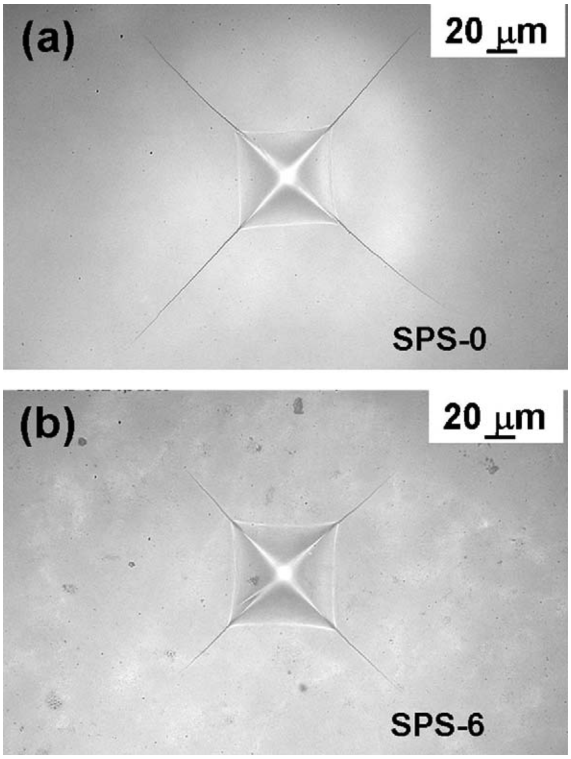

Fig. 1. Micrographs of the Vickers indentations in the samples, 24 h after indentation where it can be seen that the cracks have fully developed: (a) SPS-0 and (b) SPS-3.

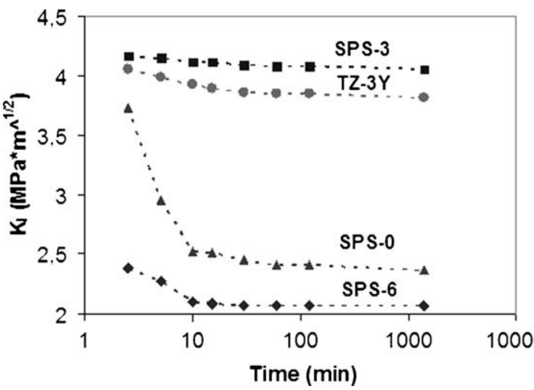

Fig. 2. Evolution of the stress intensity factor (K_I) versus time for the different materials.

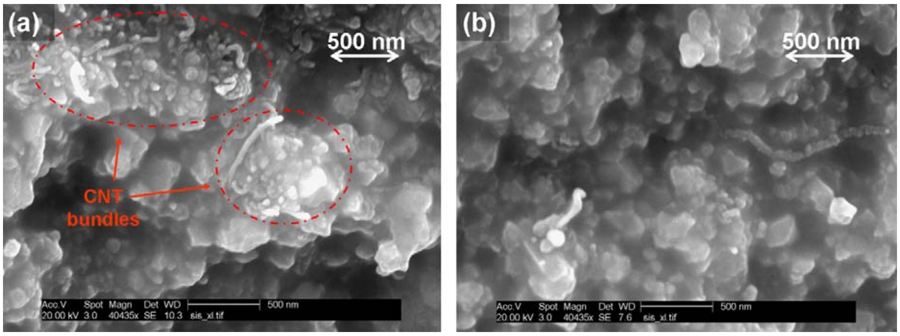

Fig. 3. HRSEM images of comparison of (a) the heterogeneous dispersion of SPS-6 and (b) the homogeneous dispersion of SPS-3.

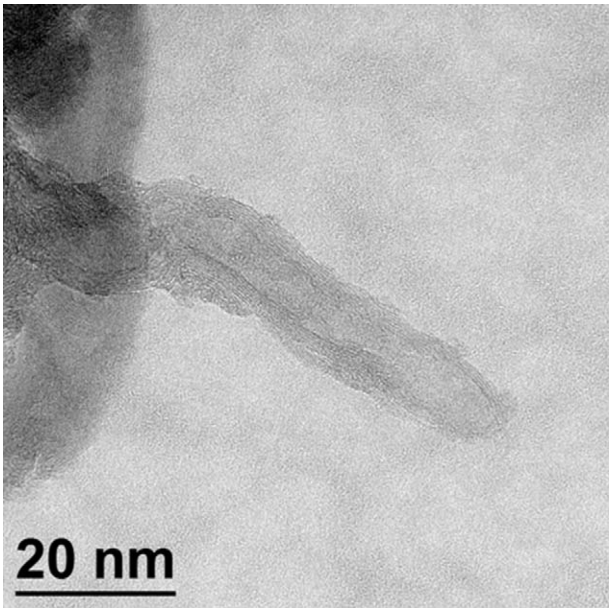

Fig. 4. TEM image of a SPS-3 sample with a MWCNT coming out of the nanocomposite.

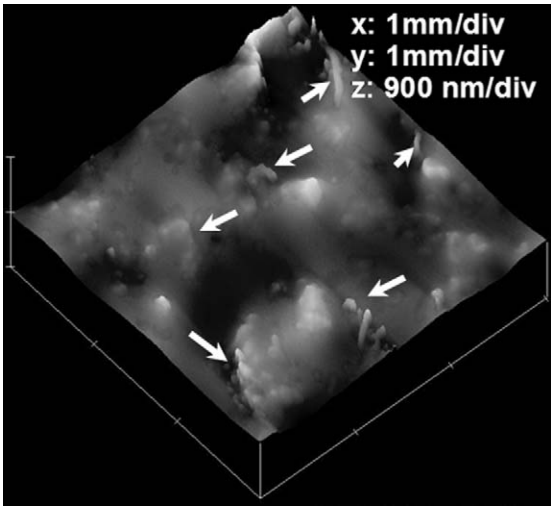

Fig. 5. AFM image of a SPS-3 sample showing the carbon nanotube pull-out on the fracture surface.

higher amount of CNT, SPS-6, do not show any improvement on the toughness, but a decrease when compared to the samples without nanotubes, SPS-0. This seems to be due to the heterogeneous dispersion of CNT in the matrix and the presence of large CNT agglomerates, as shown in Fig. 3a. The lack of a well dispersed CNT net prevents its toughening action. On the contrary, the SPS-3 samples presented high values of threshold stress intensity factor, even higher than those of the conventional yttria-stabilized zirconia sample (TZ-3Y). This suggests that the addition of the partially coated nanotubes has a reinforcement effect on the fine grained zirconia as long as there is a good dispersion (Fig. 3b). The stability of the MWCNT in the SPS-3 and SPS-6 samples after the SPS was proved with the observation of the samples in the TEM. Fig. 4 shows the TEM image of a SPS-3 sample with a MWCNT coming out of the nanocomposite. By AFM (Atomic Force Microscopy) the fracture surface of the SPS-3 was studied (Fig. 5). The carbon nanotube pull-out in the fracture surfaces of the samples is visible. This is also one of the toughening mechanisms of the zirconia-MWCNT

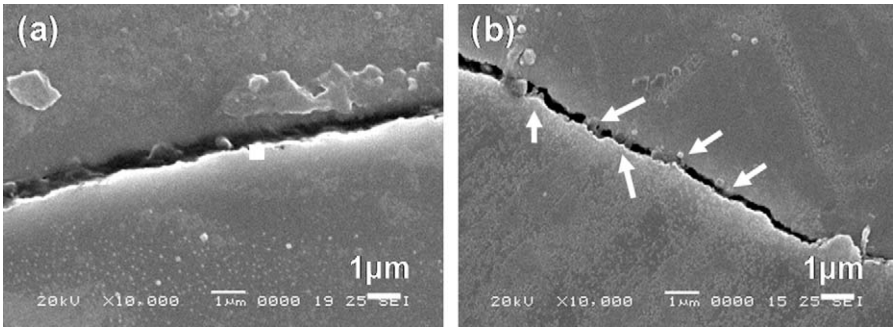

Fig. 6. SEM images of the Vickers indentation cracks in the (a) SPS-0 samples and (b) SPS-3 samples.

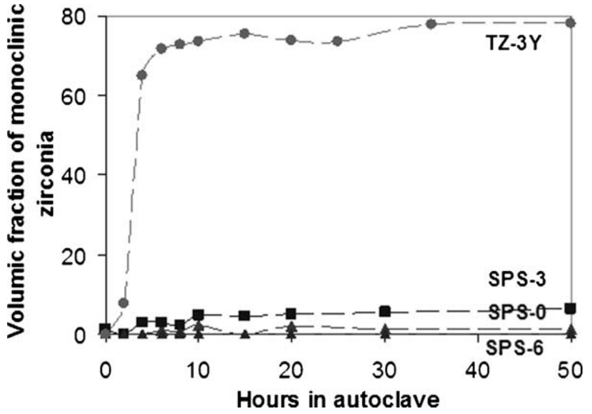

Fig. 7. Monoclinic phase fraction evolution of the studied samples.

nanocomposites cited in the literature.[13–15] By SEM (Scanning Electron Microscopy) the Vickers indentation cracks of the SPS-0 and SPS-3 were observed and compared (Fig. 6). While for the samples without CNT, SPS-0, no bridging is observed, for the samples with CNT, SPS-3, zirconia coated MWCNT bridges can be observed, another toughening mechanism.[13–15]

The low temperature degradation or ageing of the yttria-stabilized zirconia has been the subject of study of many authors.[4,33–38] The ageing kinetics of the samples was measured by X-ray diffraction. In Fig. 7 the volume fraction of the monoclinic phase is presented as a function of the ageing time. After 50 h of low temperature degradation (which simulates more than 150 years of in vivo performance),[38] the SPS sintered samples showed nearly no evidence of ageing (less than 5% of monoclinic volume fraction for the SPS-3 samples) or even no ageing was observed (for the SPS-0 and SPS-6 samples). On the other hand, the TZ-3Y samples showed 78% of monoclinic volume fraction after 50 h of treatment. This saturation was reached after 35 h of autoclave treatment, in good agreement with the references for this kind of material.[37] For the samples sintered by SPS it seems that no phase transformation is produced, thanks to the smaller grain size of both the samples with and without MWCNT. To corroborate this extent, samples were fractured with an impact and the fracture surfaces were studied by XRD. For the TZ-3Y samples a volumetric monoclinic transformation of 15% was observed. For the SPS sintered samples no transformation was observed, except for the SPS-3 samples, where 7.5% of monoclinic phase was measured.

4. Conclusions

The addition of a small volume fraction of partially coated MWCNT in a polycrystalline, nano-structured Y-TZP, sintered by Spark Plasma Sintering, results in a material exhibiting an exceptional balance between ageing and crack resistance. This balance is possible thanks to the small grain size of the sintered zirconia matrix (obtained by the SPS sintering process), which impedes the phase transformation that characterizes the ageing. But the loss in the transformation toughening mechanism of yttria-stabilized zirconia is compensated by the addition of MWCNT with a bond to the zirconia. New toughening mechanisms (bridging and CNT pull-out) which increase the toughness of the nanozirconia matrix have been observed.

Acknowledgements

This work was supported by the Basque Government (BF105.R2.555 and Etortek: Nanomaterials). The authors would also like to acknowledge Dr. Jordi Arbiol from the Universitat de Barcelona (Spain) for the TEM images.

References

1. Gupta TK, Lange FF, Bechtold JH. Effect of stress-induced phase-transformation on properties of polycrystalline zirconia containing metastable tetragonal phase. *J Mater Sci* 1978;**13**:1464–70.
2. Deville S, Gremillard L, Chevalier J, Fantozzi G. A critical comparison of methods for the determination of the aging sensitivity in biomedical grade yttria-stabilized zirconia. *J Biomed Mater Res B: Appl Biomater* 2005;**72**:239–45.
3. Chevalier J. What future for zirconia as a biomaterial? *Biomaterials* 2006;**27**:535–43.
4. Garvie RC. The occurrence of metastable tetragonal zirconia as a crystallite size effect. *J Phys Chem* 1965;**69**:1238–43.
5. Shukla S, Seal S. Mechanisms of room temperature metastable tetragonal phase stabilisation in zirconia. *Int Mater Rev* 2005;**50**:1–20.
6. Iijima S. Helical microtubules of graphitic carbon. *Nature* 1991;**354**:56–8.
7. Curtin WA, Sheldon BW. CNT-reinforced ceramics and metals. *Mater Today* 2004;**7**:44–9.
8. Duszová A, Dusza J, Tomásek K, Morgiel J, Blugan G, Kuebler J. Zirconia/carbon nanofiber composite. *Scripta Mater* 2008;**58**:520–3.
9. Xia Z, Riester L, Curtin WA, Li H, Sheldon BW, Liang J, et al. Direct observation of toughening mechanisms in carbon nanotube ceramic matrix composites. *Acta Mater* 2004;**52**:931–44.
10. Zhu YF, Shi L, Liang J, Hui D, Lau KT. Synthesis of zirconia nanoparticles on carbon nanotubes and their potential for enhancing the fracture toughness of alumina ceramics. *Composites B* 2008;**39**:1136–41.
11. Peigney A, Laurent Ch, Rousset A. Synthesis and characterization of alumina matrix nanocomposites containing carbon nanotubes. *Key Eng Mater* 1997;**132–6**:743–6.
12. Padture NP. Multifunctional composites of ceramics and single-walled carbon nanotubes. *Adv Mater* 2009;**21**:1767–70.
13. Sun J, Gao L, Iwasa M, Nakayama T, Niihara K. Failure investigation of carbon nanotube/3Y-TZP nanocomposites. *Ceram Int* 2005;**31**:1131–4.
14. Duszová A, Dusza J, Tomásek K, Blugan G, Kuebler J. Microstructure and properties of carbon nanofibre/zirconia composite. *J Eur Ceram Soc* 2008;**28**:1023–7.
15. Ukai T, Sekino T, Hirvonen A, Tanak N, Kusunose T, Nakayama T, et al. Synthesis and densification of CNTs/Fe/Al_2O_3 nanocomposite powders by chemical vapor deposition. *Key Eng Mater* 2006;**317–8**:661–4.
16. Garmendia N, Bilbao L, Múñoz R, Imbuluzqueta G, García A, Bustero I, et al. Zirconia coating of carbon nanotubes by a hydrothermal method. *J Nanosci Nanotechnol* 2008;**8**:5678–83.
17. Sanchez-Paisal Y, Sanchez-Portal D, Garmendia N, Muñoz R, Obieta I, Arbiol J, et al. Zr-metal adhesion on graphenic nanostructures. *Appl Phys Lett* 2008;**93**:053101.
18. Garmendia N, Arteche A, García A, Bustero I, Obieta I. XRD Study of the Effect of the processing variables on the synthesis of nanozirconia in the presence of MWCNT. *J Compos Mater* 2008;**43**:247–56.
19. Garmendia N, Santacruz I, Obieta I, Moreno R. Slip casting of nanozirconia/MWCNT composites using a heterocoagulation process. *J Eur Ceram Soc* 2009;**29**:1939–45.
20. Lawn B. *Fracture of brittle solids*. Cambridge: Cambridge University Press; 1993.
21. Anstis GR, Chantikul P, Lawn BR, Marshall DB. A critical evaluation of indentation techniques for measuring fracture toughness: I. direct crack measurement. *J Am Ceram Soc* 1981;**64**:533–8.

22. Garvie RC, Nicholson PS. Phase analysis in zirconia system. *J Am Ceram Soc* 1972;**55**:303–5.
23. Toraya H, Yoshimura M, Somiya S. Calibration curve for quantitative analysis of the monoclinic-tetragonal ZrO_2 system by X-ray diffraction. *J Am Ceram Soc* 1984;**67**:C119–21.
24. Jiang D, Thomson K, Kuntz JD, Ager JW, Mukherjee AK. Effect of sintering temperature on single-wall carbon nanotube toughened alumina-based composite. *Scripta Mater* 2007;**56**:959–62.
25. Padture NP, Curtin WA. Comment on “Effect of sintering temperature on a single-wall carbon nanotube-toughened alumina-based composite”. *Scripta Mater* 2008;**58**:989–90.
26. Jiang D, Mukherjee AK. Response to comment on “Effect of sintering temperature on single-wall carbon nanotube toughened alumina-based nanocomposite”. *Scripta Mater* 2008;**58**:991–3.
27. Liang KM, Torrecillas R, Orange G, Fantozzi G. Determination of K_{ISCC} by indentation in ceramics. *J Mater Sci* 1990;**25**:5077–80.
28. Gatto A. Critical evaluation of indentation fracture toughness measurements with Vickers indenter on a ceramic matrix composite tools. *J Mater Process Technol* 2006;**174**:67–73.
29. Benzaid R, Chevalier J, Saâdaoui M, Fantozzi G, Nawa M, Diaz LA, et al. Fracture toughness, strength and slow crack growth in a ceria stabilized zirconia–alumina nanocomposite for medical applications. *Biomaterials* 2008;**29**:3636–41.
30. Chevalier J, Deville S, Fantozzi G, Bartolomé JF, Pecharroman C, Moya JS, et al. Nanostructured ceramic oxides with a slow crack growth resistance close to covalent materials. *Nano Lett* 2000;**5**:1297–301.
31. De Aza AH, Chevalier J, Fantozzi G, Schehl M, Torrecillas R. Slow-crack-growth behavior of zirconia-toughened alumina ceramics processed by different methods. *J Am Ceram Soc* 2003;**86**:115–20.
32. Basu B. Toughening of yttria-stabilized tetragonal zirconia ceramics. *Int Mater Rev* 2005;**4**:239–56.
33. Rahaman M, Yao A. Ceramics for prosthetic hip and knee joint replacement. *J Am Ceram Soc* 2007;**90**:1965–88.
34. Clarke IC, Manaka M, Green DD, Williams P, Pezzoti G, Kim YH, et al. Current status of zirconia used in total hip implant. *J Bone Joint Surg Am* 2003;**85**:73–84.
35. Schubert H, Frey F. Stability of Y-TZP during hydrothermal treatment: neutron experiments and stability considerations. *J Eur Ceram Soc* 2005;**25**:1597–602.
36. Sato T, Shimada M. Transformation of yttria-doped tetragonal ZrO_2 polycrystals by annealing in water. *J Am Ceram Soc* 1985;**68**:356–9.
37. Lange FF, Dunlop GL, Davis BI. Degradation during aging of transformation toughened $ZrO_2–Y_2O_3$ materials at 250 °C. *J Am Ceram Soc* 1986;**69**:237–40.
38. Chevalier J, Cales B, Drouin JM. Low temperature aging of Y-TZP ceramics. *J Am Ceram Soc* 1999;**82**:2150–4.