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Original Article

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

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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.
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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

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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°.

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