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# Colloidal processing of fully stabilized zirconia laminates comprising graphene oxide-enriched layers

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ABSTRACT

Multilayer materials have demonstrated to provide an efficient mechanism for toughening by deflection of a propagating crack by weak interlayers. Therefore, the aim of this work is to study the colloidal processing of 8 mol% yttria stabilized zirconia (8YSZ) based laminates by intercalating thin layers of graphene enriched with 8YSZ, and to evaluate the advantages of such multilayered structure in the propagation of cracks induced by indentation. Green tapes of 8YSZ and graphene-oxide with YSZ were obtained by aqueous tape casting and sintered in one-step by spark plasma sintering at 1400 °C. Microindentation results showed that the indentation cracks propagate within the horizontal direction within the ceramic layer, but in the cross-sectional direction the presence of the GO-rich layers stops the cracks without deflection or bifurcation. The hardness and elastic modulus values were higher than 17.6 GPa and 230 GPa, respectively, and similar for all layers.



## 1. Introduction

8 mol% yttria stabilized zirconia (8YSZ) has been extensively used as an electrolyte because of its low electronic and high oxide ion conductivity over wide ranges of temperature and oxygen partial pressure, as well as excellent chemical stability under reduced and oxidized atmospheres at a high temperature. These properties make 8YSZ a powerful material for applications as oxygen sensors and solid oxide fuel cells [1–5]. The basic structure of a solid oxide fuel cell (SOFC) comprises at least three layers of ceramics or cermet: i.e., electrolyte, anode and cathode layers [6,7]. The electrolyte is a dense ceramic, typically yttria stabilized zirconia (YSZ) or gadolinium doped ceria (CGO), whereas the electrodes must be porous and can be either a ceramic or a cermet. Typical anode materials are Ni-YSZ and Ni-CGO while LSM (La, Sr, Mn oxide)-YSZ and LSCF (La, Sr, Co, Fe oxide) are the most frequently used as cathode materials [8–10]. The most important designs for SOFCs include tubular and planar configurations [11,12]. Among them, the anode-supported planar configuration is probably the most extensively used. Planar cells are fabricated by considering the different layers (electrode and electrolytes) produced by different techniques, such as tape casting and screen printing, which are the most suitable to produce large surfaces and fast, low cost mass production. Because of the multi-layer nature of the cells, any mismatch in the free sintering kinetics of the individual layers leads to stress and distortion during the sintering process [13–15]. Hence, the electrolyte layer must have high fracture strength and toughness, good thermal conductivity and a thermal expansion coefficient similar to that of the other components. Fully stabilized zirconia has not the excellent mechanical properties that partially stabilized zirconia has so that the development of strengthening mechanisms is strongly desired to meet the requirements of SOFCs.

The main reinforcing mechanisms for zirconia ceramics are those based on the phase transformation of zirconia from tetragonal to monoclinic induced by mechanical stresses, and the use of composites with second phase particles, whiskers, platelets or fibers and, more recently, the development of ceramic matrix nanocomposites is receiving great attention [16–19]. The use of such nanocomposites has shown to significantly enhance the mechanical properties even at high temperatures. For example, the fracture strength and creep resistance of $Al_2O_3$ were improved by

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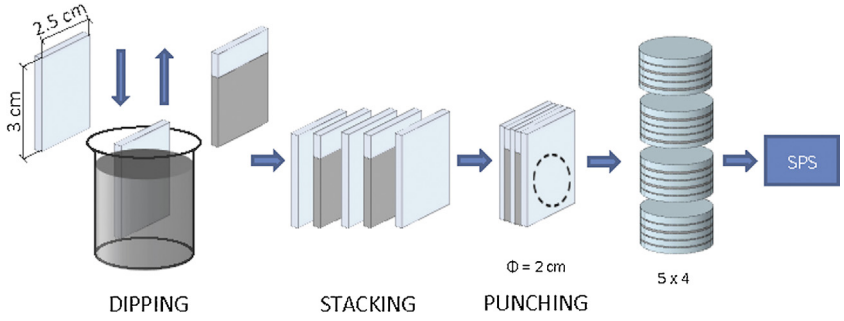


**Fig. 1.** Schematic flow chart showing the dip-coating, the stacking, the punching process that allows the conformation of the different architectures and then, the SPS process.

3–5 times and by 3–4 orders, respectively, by incorporating only 5% nano-sized SiC particles [20].

Another route for reinforcing the properties of ceramics that is receiving increased interest is the use of composites containing carbon nanodispersoids such as carbon nanotubes (CNTs), carbon nanofibers (CNFs) or graphene. The incorporation of such carbonaceous derivatives have demonstrated to improve the electrical and dielectric properties of the composites after reduction to reduced graphene during the thermal treatment under vacuum, hot pressing (HP) or spark plasma sintering (SPS), but its efficiency as a strengthening agent is still controversial [21–25]. For example, the main factors responsible for the inhomogeneous dispersion of CNTs in the ceramic matrix are the weak interfacial bonding between CNTs and ceramic grains, and the damage of CNTs during high temperature processing. Some strategies have been developed to improve the dispersion of the carbon nanodispersoids and the homogeneity of the sintered materials such as heterocoagulation, colloidal dispersion, acid treatments and sonication, among others [26–29].

Graphene oxide (GO) is easily dispersible in water so that uniform GO-ceramic composites with homogeneous microstructures can be obtained. However the mechanical properties expected for GO-ceramic composites are not as good as required, at least for bulk materials. Some publications on graphene reinforced yttria-partially stabilized zirconia composites obtained by SPS have been recently reported [30,31]. Shin et al. obtained fully densified reduced GO-YSZ composites with improved electrical conductivity and fracture toughness, but hardness decreased with reduced GO addition. Liu et al. reported the preparation of graphene platelets-zirconia-toughened alumina (GPLs-ZTA) composites in which an addition of 0.81 vol% GPLs into the ZTA composite resulted in a 40% increase in fracture toughness. They also found that the hardness decreased with the introduction of GPLs as a minor phase.

An effective way for enhancing the properties of ceramic-based composites is to produce laminates with tailored distribution and thickness of the layers. Multilayer materials have demonstrated to provide an efficient mechanism for toughening by either the deflection of a propagating crack by weak interlayers or by designing strongly joined interfaces where an alternate tensile-compressive residual stress state may arise during cooling from sintering. A broad body of work has been published concerning the processing, sintering, and mechanical performance of zirconia-toughened laminates focusing the key role of the residual stresses on the fracture behavior [32–36].

Colloidal processing allows to obtain uniform dispersion of different phases with high reliability and through simple processing methods [37,38]. In particular, great effort is being developed in order to obtain uniform microstructures with a good dispersion of the nanodispersoids by controlling the colloidal and rheological behavior of the mixtures [39,40]. In previous works, the preparation of $Al_2O_3$-3YTZP-graphene multilayer materials combining tape casting and fast spark plasma sintering technique with good cohesion between layers and high hardness and Young's modulus values has been reported [41–43].

However, the processing, sintering and mechanical properties of fully stabilized zirconia (8YSZ) reinforced with carbon derivatives have not been studied in detail. In this case the preparation of laminates containing GO could be an attractive route to introduce weak interfaces capable to reduce the residual stresses and to improve the mechanical resistance of the stack in the cells. The aim of this work is to study the colloidal processing of 8YSZ-based laminates by intercalating thin layers of GO-enriched with 8YSZ,

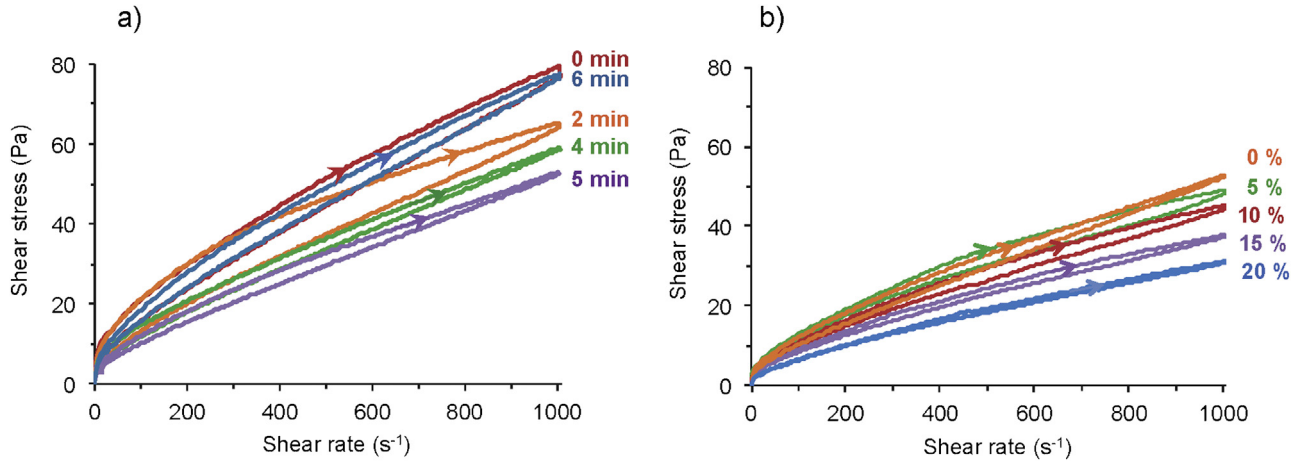


**Fig. 2.** Flow curves of suspensions of 8YSZ (45 vol% solids) prepared at different sonication (US) times (a) and of suspensions of 8YSZ after the addition of different amounts of binder in wt% (b).

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